MEMAC

MARINE HAZARDOUS NOXIOUS SUBSTANCES (HNS)

MANUAL

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By: Marine Emergency Mutual Aid Centre (MEMAC)

Foreword

The Kuwait Regional Convention (23rd April 1978) is a comprehensive umbrella agreement for protection of the marine environment. By ratifying the Protocol (24th April 1978) concerning Regional Co-operation in Combating Pollution by Oil and other Harmful Substances in Cases of Emergency, the States of the Region introduce (24th April 1978) more specific obligations to control pollution from a discrete source, or to co-operate in various aspects of environmental management.

This comprehensive Manual has been prepared in accordance with the Marine Emergency Mutual Aid Centre functions set by the Protocol Article III – 3 (c) and all the information provided herewith is based on the Protocol and the ROPME Council Decisions.

The HNS Manual contains information needed for joint pollution combating operations, and to be used as a guideline concerning incident management, policy and strategy. The manual has been tailored to the needs of the Region avoiding duplications and repetition of standard information which already exists and fulfills the requirements.

MEMAC, the Marine Emergency Mutual Aid Centre, is responsible for regional co-operation on marine pollution preparedness and response in the region, has also the responsibility to develop, update and maintain this plan as it deem appropriate.

With technical support from the International Maritime Organization (IMO), MEMAC is currently functioning as secretariat and Expert Meeting, Competent National Authorities Meeting (Oil and HNS Spill Response Officer) for RSA Regional Oil Spill Contingency Plan meeting. The centre also carries out other special activities including the management of a regional information system, organization of training and exercise, capacity building, co-ordination of research and development on the technical aspects of oil and Hazardous & Noxious Substances (HNS) spills.

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Chapter1.

Introduction

The OPRC-HNS Protocol follows the principles of the International Convention on Oil Pollution Preparedness, Response and Co-operation, known as the OPRC Convention. The OPRC-HNS Protocol was formally adopted by IMO member States, who were already signed up to the OPRC Convention at a Diplomatic Conference held at the IMO headquarters in London in March 2000.

Like the OPRC Convention, the HNS Protocol aims to provide a global framework for international co-operation in combating major incidents or threats of marine pollution from Hazardous and Noxious Substances. Countries that sign up to the HNS Protocol will be required to establish National, Regional and International preparedness, response and cooperation measures for dealing with HNS pollution incidents. Similar to the OPRC Convention, ships carrying HNS will be required to carry a shipboard pollution emergency plan to deal specifically with incidents involving HNS, in a similar way that they have shipboard pollution emergency plans for dealing with oil pollution.

For the purpose of the OPRC-HNS Protocol, HNS means any substance other than oil, which, if introduced into the marine environment is likely to create hazards to human health, to harm living resources and marine life, to damage amenities or to interfere with other legitimate uses of the sea.

The IMDG Code gives more than 3000 United Nations Numbers for the purpose of substance identification, about 200 of these are for ‘Generic’ or ‘Not Otherwise Specified (NOS)’ substances, and these numbers are the most commonly used when goods are being transported. For all goods shipped as ‘NOS’, a recognised chemical name in current use and readily available in scientific and technical handbooks should be given, while trade names alone should not be used.

In recent years, there has been a rapid growth in the transportation of HNS. If allowed to escape, these substances can present a significant danger to the vessel, its crew, coastal and harbour populations, and the surrounding environment.

There are many types of ships that can and do carry HNS:

· Dry bulk carriers: solid bulk cargoes, e.g. ores, fishmeal, manufactured powders.

· Oil/bulk/ore or combo carriers: multi-purpose carriers of solid or liquid cargoes.

· Containerships: boxes for dry cargo, powders and/or liquids in portable ISO tanks.

· General cargo ships: cargo in consignments e.g. crates, boxes, drums, sacks, bags.

· Roll-on/roll-off ferries: road vehicles carrying internally unitised, packaged or bulk cargoes.

· Chemical carriers: specialised vessels designed to carry liquid chemicals in bulk.

· Gas carriers: specialised vessels designed to carry liquefied gas.

The International Maritime Dangerous Goods (IMDG) Code describes how to pack, label, document, transport, stow and segregate dangerous goods in packages.

Many incidents involving HNS are relatively minor: leaking drums, broken glass, failed packaging and similar. In cases such as these, there is a tendency to call upon the local fire brigade or response contractor to make the site safe, contain the suspect package and then remove it in an overdrum or tranship it into another suitable package.

HNS is also mentioned in another convention, known confusingly as the HNS 1996 Convention, which as the date suggests was adopted earlier than the OPRC 200 Protocol, but it too has not yet come into force.

The International Convention on Liability and Compensation for Damage in Connection with the Carriage of Hazardous and Noxious Substances (HNS) by sea, known as the HNS 1996 Convention, provides for a compensation and liability regime for incidents involving HNS.

The simple difference is that the HNS Convention deals with compensation from HNS, whilst the HNS Protocol deals with preparedness and response measures for dealing with HNS spills.

Similarly there is compensation for oil pollution incidents that are covered by an International Civil Liability Convention for Oil Pollution Damage, and by an International Fund Convention for Compensation for Oil Pollution Damage, both in turn are supplemented by Protocols.

A major difference is that HNS can kill and be radically more harmful and toxic than oil. A 100 litre spill of toxic chemical can do more harm than a 100 litre heavy fuel oil spill.

Another difference is that oil is in a liquid form, although of varying viscosities, whilst HNS can come in solid, liquid or gas forms. Therefore consideration in the different types of operational handling and modes of transport of HNS will impact upon considerations of how to handle a HNS incident.

HNS incidents do not necessary have to be an uncontrolled release of cargo from a ship onto the water as an oil spill is invariably considered. The HNS incident can be during cargo handling or transportation of a HNS which is a liquid, solid or gas form, and either stays immobile or moves or changes state.

The HNS can start out in one form and evolve into another form by changing conditions acting upon the released or contained HNS, which in turn has implications on the surrounding community, workers and response personnel.

The risk of an uncontrolled release of a HNS is one or more of the following:

Explosion, **F**ire, **R**eactivity, **T**oxicity

Organisations must therefore make every **EFRT** (said as effort) to prevent an HNS incident from happening, and should it do so, to have in place a level of preparedness to be able to take the right action to minimise the immediate and long-term effects on the community and surrounding property. As in all response matters, preparation, preparation and preparation in that order will be the most effective tools for dealing with an HNS incident.

International Maritime Organization (IMO) estimates that more than half of packaged goods and bulk cargoes transported by sea today can be regarded as dangerous, hazardous, or harmful to the environment. A great deal of these substances, materials and articles are also dangerous or hazardous from a human safety point of view.

ROPME Sea Area is an area with intensive marine transport of HNS. It is understood that each HNS spill presents its own particular problems for Government and industry, depending on such things as weather, type of substance, and its location. It is not possible to provide turn-key solutions that are ready to be retrieved from the guideline right at the scene of the accident, but document containing general recommendations and information will be very useful. Due to high level of hazards at chemical spills, it is necessary to have uniform policy to respond to them. As one of main outcomes of MEMAC activities, the RSA Regional Oil Contingency Plan were developed and officially came into effect as being signed by all RSA Member states. The purpose of the RSA RCP is to provide an operational mechanism for mutual assistance through which the member states will co-operate during major marine oil pollution incidents in the region In order to provide practical and technical guidelines to promptly and effectively respond to major marine pollution accidents within the framework of the RSA RCP, it was also agreed to develop the Regional HNS Contingency Plan and also Regional HNS Manual in order to tailor the need of the region to be prepared and response effectively to the HNS incident as well, taking into consideration the rapid grow of the HNS transportation in Region. The MEMAC carry out the series of Specific Projects related to oil spill prediction model, minimum level of preparedness for response to oil spill in the RSA region, HNS response operation training.

MEMAC has prepared a regional guideline with the aim to give general recommendations and provide information needed for proper decision making when responding to accidents in the marine environment involving chemicals and dangerous goods.

This, however, is not a substitute for the national guidelines and manuals on HNS spills response existing in RSA Member States. The guideline is based on provisions of existing regional and national RSA Member States manuals and recommendations. The contents of the guideline must be thoroughly reviewed beforehand. The contents are primarily aimed for personnel who are familiar with the area.

The content of MEMAC HNS Manual was based on international and other regional HNS manuals. Hazards, classification, behavior, response options, and safety measures of HNS are the main compounds.

1.2 The Aims of the Manual

The Manual is to enable the Member States to establish prompt and effective response measures to HNS and any other harmful substances spilled at sea at National or Regional level.

The manual is also the practical tool intended to assist:

- Provide timely information to the decision makers and various Command levels.
- The On-Scene Commanders in the execution of response operations.
- Providing instant and adequate information reference to the decision makers in the execution of a joint combating operation involving other Member States.
- Provide an overview of practical response measures which are available to deal with HNS spills.

1.3 Manual Preparation Method

i) The Pollution Manual has been prepared in a number of subjects and indicated by reference numbers and sub reference numbers.

ii) Each page footer indicates the Manual name and year on the left-hand side, and page number on the right-hand side.

iii) Whenever there is any update for the existing information, the pages will be changed

iv) In case of replacing any of the existing pages or adding extra pages to the Manual, the replaced pages or the additional pages should take the existing number or the sequence number of the new added pages correspondingly. *i.e.* 6/1, 6/2 . and so on.

v) Whenever any new information or data provided, the new sector should be inserted within its relative category of information and will follow the existing sequences of sub numbering.

1.4 Date of the Manual

The Manual has been prepared by MEMAC and revised by the Member States Oil Spill Response Officers according to the data available up to 2013.

1.5 Updating the Manual

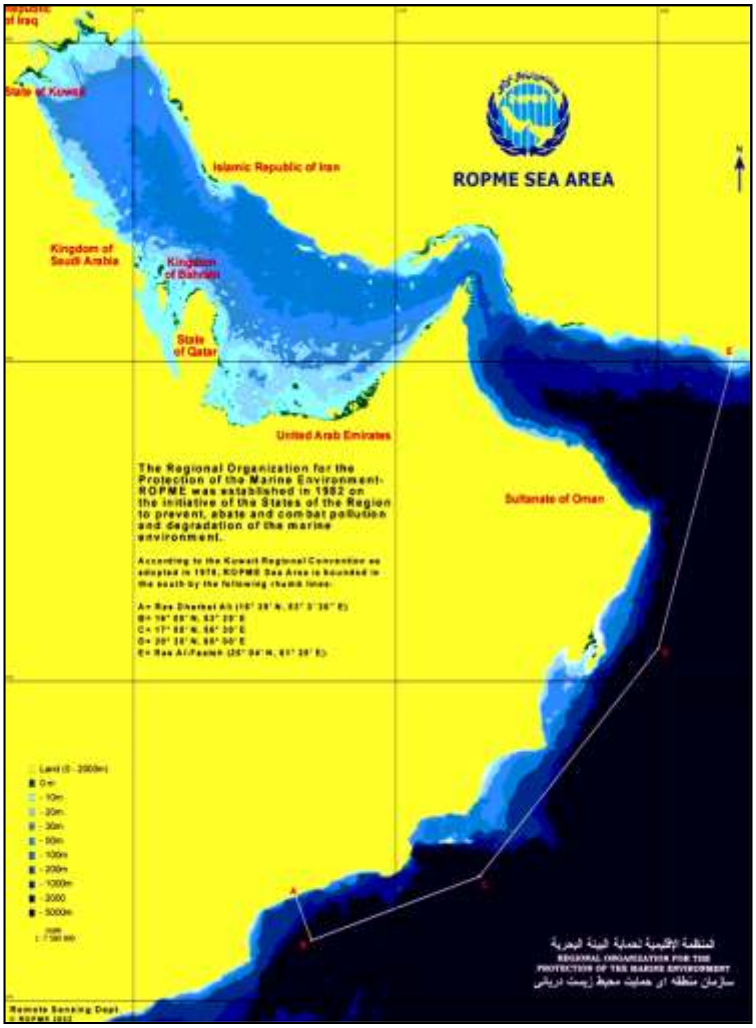
The updating of the Manual will take place according to the data and information received from the Member States and whenever necessary. Further, the update and the additional information needed for this Manual should be discussed and recommended by the Oil Spill Response Officers and to be approved by the ROPME Council.

1.6 The Geographical Coverage

The coverage area is the ROPME Sea Area as identified by the Kuwait Regional Convention for Co-operation on the protection of the Marine Environment from Pollution, Article II (a).

Article II

(a) The present Convention shall apply to the sea area in the Region bounded in the south by the following rhumb lines: from Ras Dharbat Ali (l6^{o} 39' N, 53^{o} 3’ 30’’ E, to a position l6^{o} 00' N, 53^{o} 25’ E; thence through the following positions: 17^{o} 00' N, *56*^{o} 30' E and 20^{o} 30' N, 60^{o} 00' E to Ras Al-Fasteh (25^{o} 04' N, 61^{o} 25' E). (Hereinafter referred to as the "Sea Area".)



The Regional Organization for the Protection of the Marine Environment-ROPME was established in 1982 on the initiative of the States of the Region to prevent, abate and combat pollution and degradation of the marine environment.

According to the Kuwait Regional Convention as adopted in 1978, ROPME Sea Area is bounded in the south by the following rhumb lines:

1.7 Member States Coastal Line Length

States	Km	n. miles	States	Km	n. miles
K. Bahrain	183.5	100	S. Oman	2386	1300
I. R. Iran	2782	1516	Qatar	642	350
R. Iraq	66	36	K. Saudi Arabia	2160	1560
Kuwait	569	310	UAE	1246	900

Note: The length of the coasts is given approximately, where the coast length of some of the Member States may increase due to reclamation.

1.8 The Protocol

In accordance with the provision of the Protocol concerning Regional Co-operation in Combating Pollution by Oil and other Harmful Substances in Cases of Emergency Article II and XI, Where Article II states that:

> 1. The Member States shall co-operate in taking the necessary and effective measures to protect the coastline and related interests of one or more of the States from the threat and effects of pollution due to the presence of oil or other harmful substances in the marine environment resulting from marine emergencies.
>
> 2. The Member States shall endeavour to maintain and promote, either individually or through bilateral or multilateral co-operation, their contingency plans and means for combating pollution in the Sea Area by oil and other harmful substances. These means shall include, in particular, available equipment, ships, aircraft and manpower prepared for operations in cases of emergency.

And Article XI states that:

> 1. Any Member State requiring assistance in a marine emergency response may call for assistance directly from any other Member State or through the Centre. Where the services of the Centre are utilized, the Centre shall promptly transmit requests received to all other Member States. The Member States to whom a request is made pursuant to this paragraph shall use their best endeavours within their capabilities to render the assistance requested.
>
> 2. The assistance referred to in paragraph 1 above may include:
>
> (a) Personnel, material, and equipment, including facilities or methods for the disposal of recovered pollutant;
>
> (b) Surveillance and monitoring capacity;
>
> (c) Facilitation of the transfer of personnel, material, and equipment into, out of, and

through the territories of the Member States.

3. The services of the Centre may be utilized by the Member States to co-ordinate any marine emergency response in which assistance is called for pursuant to paragraph I above.

4. Any Member State calling for assistance pursuant to paragraph 1 above shall report the activities undertaken with this assistance and its results to the Centre. The Centre shall promptly transmit any such report to all other Member States.

5. In cases of special emergencies, the Centre may call for the mobilization of resources made available by the Member States to combat pollution by oil and other harmful substances.

1.9 ROPME Council Decision

Furthermore and according to Article III – (b)/(iii), the ROPME Council at its Ninth Meeting decided to approve the regional Guideline of the Loan and Transboundary Movement of **Personnel, Equipment and Materials in Cases of Emergency (See Decision 24 of the Meeting).**

Chapter 2.

First actions in case of spill of chemical transported in bulk

When ship accidents and spills involving chemicals occur the incidents must be reported to all relevant bodies according to “Shipboard marine pollution emergency plan for HNS” (SMPEP), required by regulation 17 Annex II MARPOL or by national and international agreements and regulations. Persons on board shall take immediately actions to reduce or control the discharge of HNS and establish procedures and point of contact on the ship. This action is to ensure coordination of actions onboard the ship with national and local authorities in combating the pollution at sea. When responding to accidents at sea involving chemicals or dangerous goods, general first steps, at times, must be taken by responders (Figure 1). This is true for many accidents, no matter the circumstances, even if chemicals are involved.

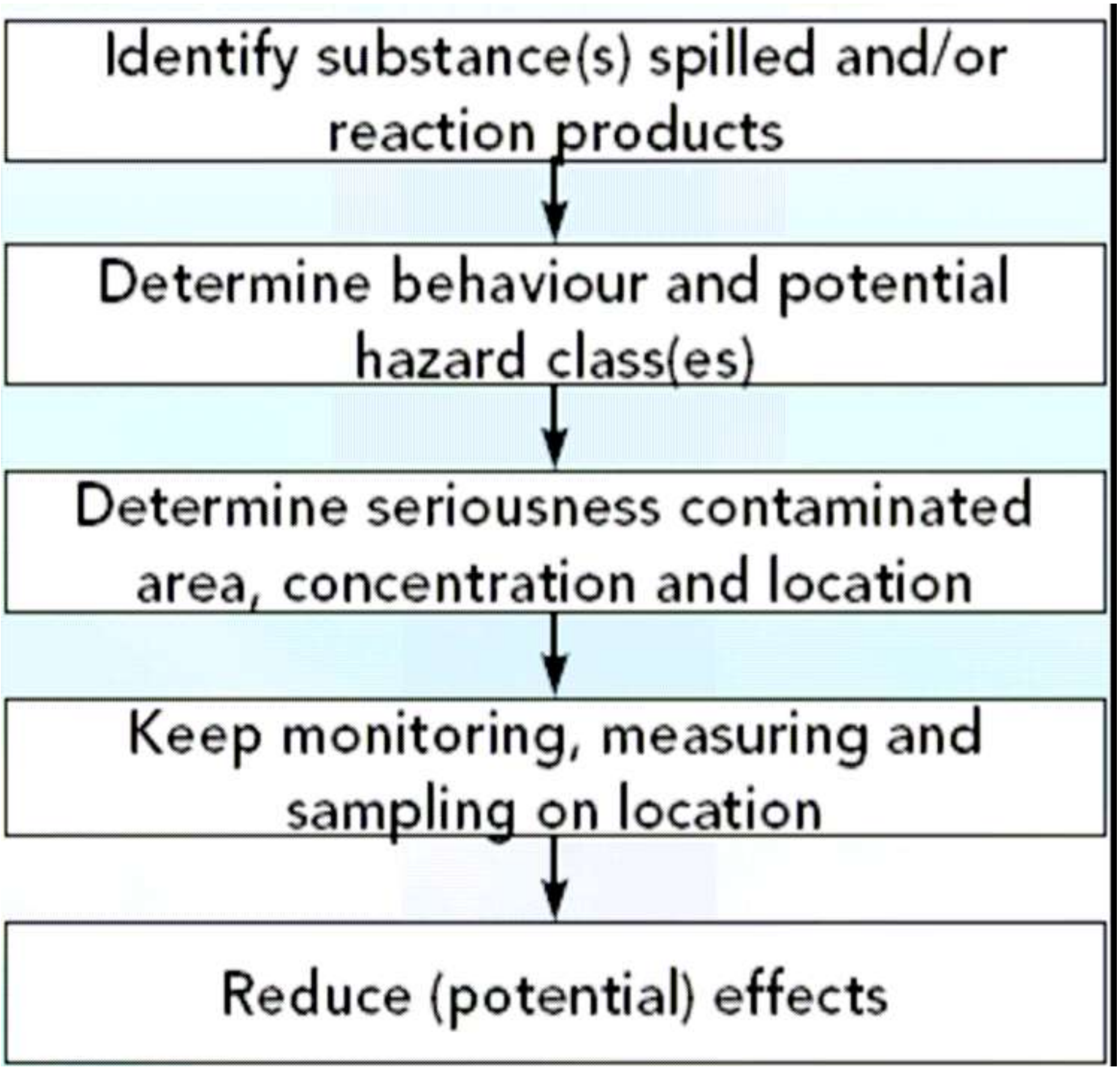


Figure 1. *Flow diagram of general approach to spills involving HNS.*

In case of HNS spill *“Never rush into a chemical incident, but try to use your common sense and assess the situation carefully (use principle “Think before you act”). It is best to plan for the worst possible scenario. Realize that each chemical is different and that a new incident is not going to be the same as an earlier one. There is no such thing as a typical incident.*

The following list of advices includes general routines that often should be applied in case of HNS spills at sea. In minor incidents, it is not necessary to follow all of the advices. It is enough to limit the extent of use. For major accidents, it might be necessary to apply the advices to the fullest possible extent. See also "Example of a checklist" in *Table 1*.

- *Get as much information as possible about the situation and a rapid general view of it. And then, judge the need for the most urgent actions to be taken, such as medical care for victims, restriction of access, evacuation, reduction of leakages, etc.*
- *Inform appropriate authorities, agencies, and mass media.*
- *Identify all the involved chemicals. Note the volume, as well as the size of spill or discharge.*
- *Assess the risk of fire, explosion, and leakage as well as health risks and risks for adjacent areas (utilize e.g. Health risk safety, Chemical safety Class, Chemical Information Databases).*
- *Establish restriction areas (risk zones) and restrict access to these areas.*
- *Make preparations for procedures regarding decontamination, relieving, and replacement of personnel, materials and equipment.*
- *Make appropriate arrangements like restriction of access or right to use for beaches, swimming areas, fishing grounds, fresh water intakes, etc.*
- *Continuously use monitoring devices for fires, explosions, and health risks.*
- *Assess emission rates, volumes, properties, and reactivity for involved chemicals.*
- *Assess initial drift, spread and evaporation (direction, distance, volumes), and calculate these behaviors by modeling programs and making forecast maps.*
- *Continuously monitor drift and spread in order to assess the risk, and continuously take appropriate actions based on the assessment.*
- *Take appropriate steps to stop or reduce damage to environment and property.*
- *Contact, as soon as possible, relevant National and Regional concerned bodies and plan for appropriate handling of the hazardous waste associated with response operations.*

In an operation at sea involving a chemical accident, it is important to follow a checklist where steps can be marked off one by one during the course of operation. The list below can be used as an example. This is from the First actions in case of spill of chemical transported in bulk National Strike Force of the United States Coast Guard and is called ***Hazardous Chemical Emergency Response Checklist****.*

Table 1. *Example of checklist*

1. Risk assessment completed...
2. PPE* selection completed...
3. Emergency Response Procedures completed..................................
4. Work zones established..
5. PPE* checks completed...
6. Decontamination line assembly completed.......................................
7. Instruments calibrated..
8. Communication plan completed..
9. Pre-entry medical monitoring completed...
10. Initial entry objectives established..
11. Action levels established...
12. Sampling plan completed...
13. Pre-entry brief completed...
14. Practice run through decontamination line..
15. Communications check..
16. Authorization for entry...
17. Post-entry medical monitoring completed...
18. Entry team debrief completed..
19. Emergency Response and Site Safety Plan modifications...............
20. Equipment decontamination/inventory completed............................
21. Contaminated materials disposed...
22. Potential Exposure Record forms completed....................................
23. Debrief conducted with OSC..

PPE = Personal Protection Equipment

Chapter 3.

Assessment of potential risk

Risk assessment is a very important part of HNS spill response. All decisions should be made based on results from the risk assessment. The following information relates to this.

- Classification of hazardous and noxious substances (HNS).
- Properties of HNS and its behavior in the environment.
- The drift and spread of chemical spills.
- Information about valuable ecosystem components, water intakes, Desalination Plant and recreational places.

3.1. Classification of hazardous and noxious substances (HNS)

The Manual is based on the accepted and used by IMO. The system is based on the physical behaviors in water (solubility, density, vapor pressure), which could therefore be responded to in a similar way. The system is comprised of 12 property groups (G, GD, E, ED, etc.) of substances and 3 groups of packages (PF, PI and PS). A schematic of the flow chart of a system for classification of chemical spills in water used to define the property groups is shown on Fig. 2 and table 2.

Table 2. *Property Group Designations for spilled chemicals in water*

G	**gas**	**FE**	**floater/evaporator**	**D**	**dissolver**
GD	**gas/dissolver**	**FED**	**floater/evaporator/dissolver**	**SD**	**sinker/dissolver**
E	**evaporator**	**F**	**floater**	**DE**	**dissolver/evaporator**
ED	**evaporator/dissolver**	**FD**	**floater/dissolver**	**S**	**sinker**

Dividing the chemicals into different subcategories (E, ED, FE, F, FD, FED, DE, D, SD, and S) can lead to a need for a relatively small number of generally applicable response options in the event of an accident. It is important to be aware of the hazards that chemicals can cause when released into the marine environment. The most important aspect of situation analysis is determining the hazards of an accidental spill, in order to prepare a plan of action.

In the event of an accident at sea, pollutants may contaminate the air, the water surface, the water column and/or the sea floor, and all the organisms in Assessment of potential risk these compartments and other users of these compartments. The degree of seriousness depends on other properties of the substance released and the fate and transport of the substance in the marine environment.

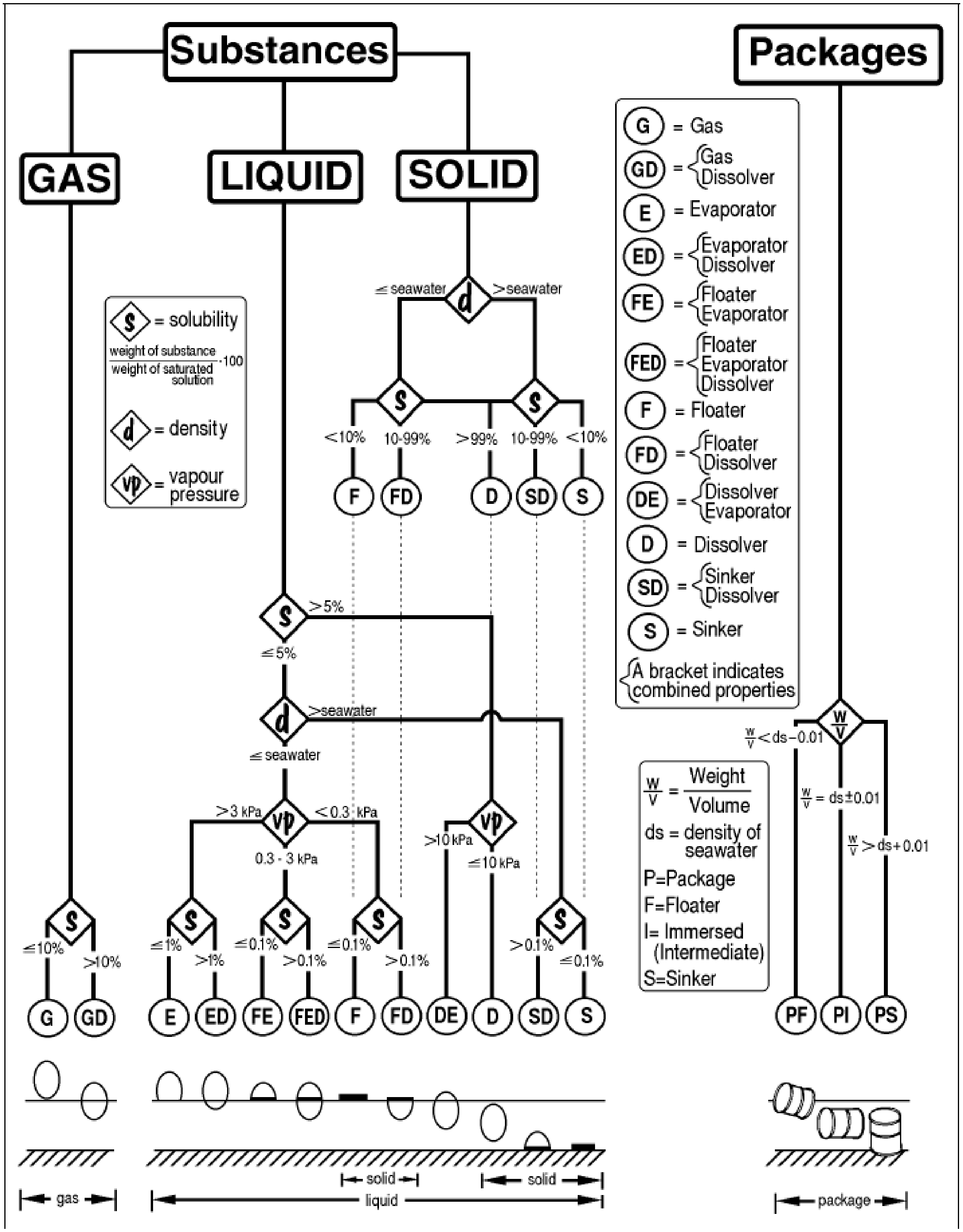
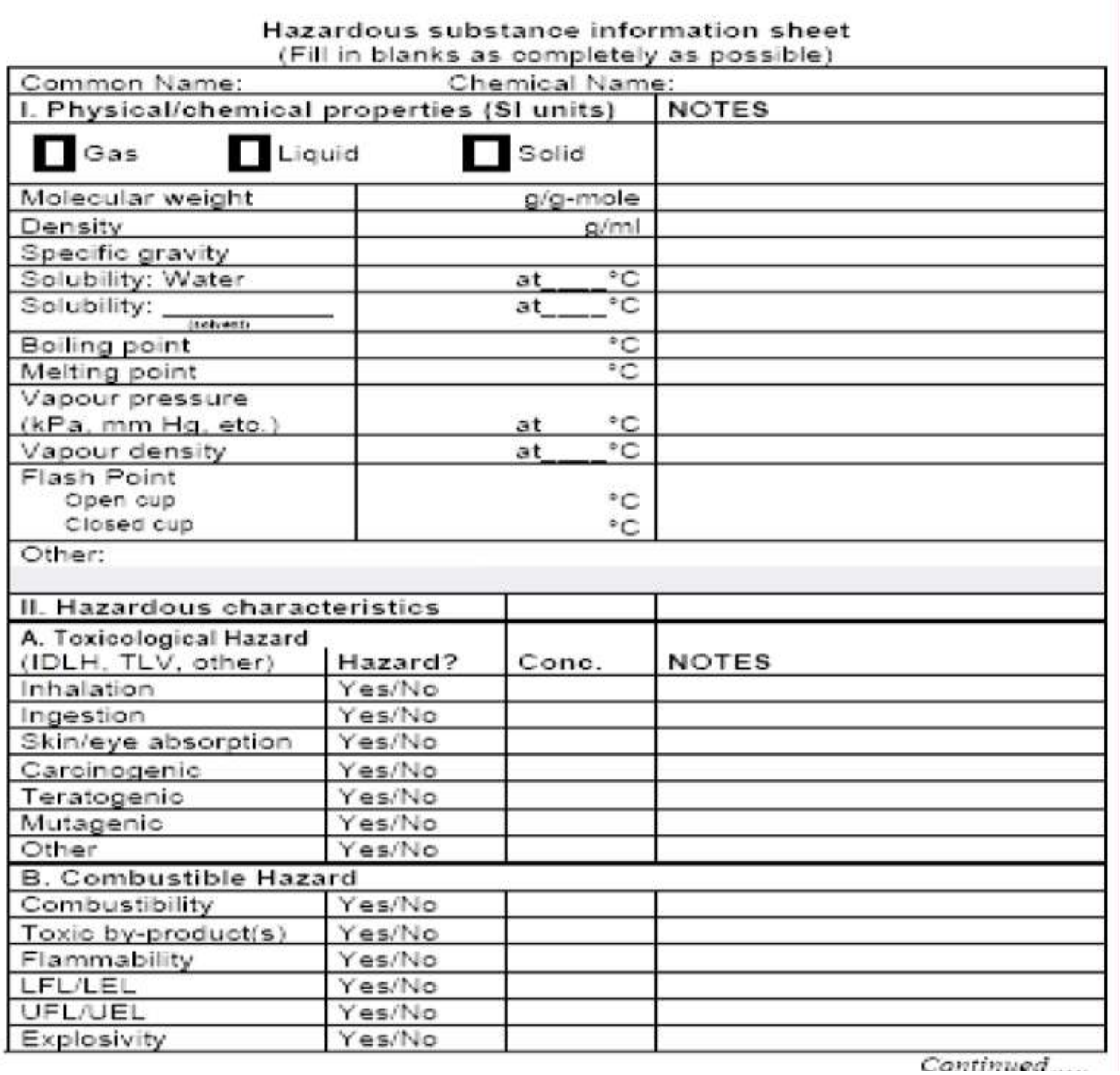


Figure 2. *Flow chart used to assign property groups in the Classification system.*

3.2. Properties of HNS

During a response to accidents involving hazardous and noxious chemicals, it is crucial to have all possible information concerning toxicity, reactivity, solubility, evaporation, corrosiveness and explosiveness of spilt substances.

This could be done by compiling the most important data from different sources into information sheets. Example is shown in Table 3



Hazardous substance information sheet

(Fill in blanks as completely as possible)

Common Name: Chemical Name:

I. Physical/chemical properties (SI units)		**NOTES**
☐ Gas ☐ Liquid ☐ Solid		
Molecular weight	g/g-mole	
Density	g/ml	
Specific gravity		
Solubility: Water	at____°C	
Solubility: ____________ (solvent)	at____°C	
Boiling point	°C	
Melting point	°C	
Vapour pressure (kPa, mm Hg, etc.)	at °C	
Vapour density	at____°C	
Flash Point Open cup Closed cup	 °C °C	
Other:		

II. Hazardous characteristics			
A. Toxicological Hazard (IDLH, TLV, other)	**Hazard?**	**Conc.**	**NOTES**
Inhalation	Yes/No		
Ingestion	Yes/No		
Skin/eye absorption	Yes/No		
Carcinogenic	Yes/No		
Teratogenic	Yes/No		
Mutagenic	Yes/No		
Other	Yes/No		
B. Combustible Hazard			
Combustibility	Yes/No		
Toxic by-product(s)	Yes/No		
Flammability	Yes/No		
LFL/LEL	Yes/No		
UFL/UEL	Yes/No		
Explosivity	Yes/No		

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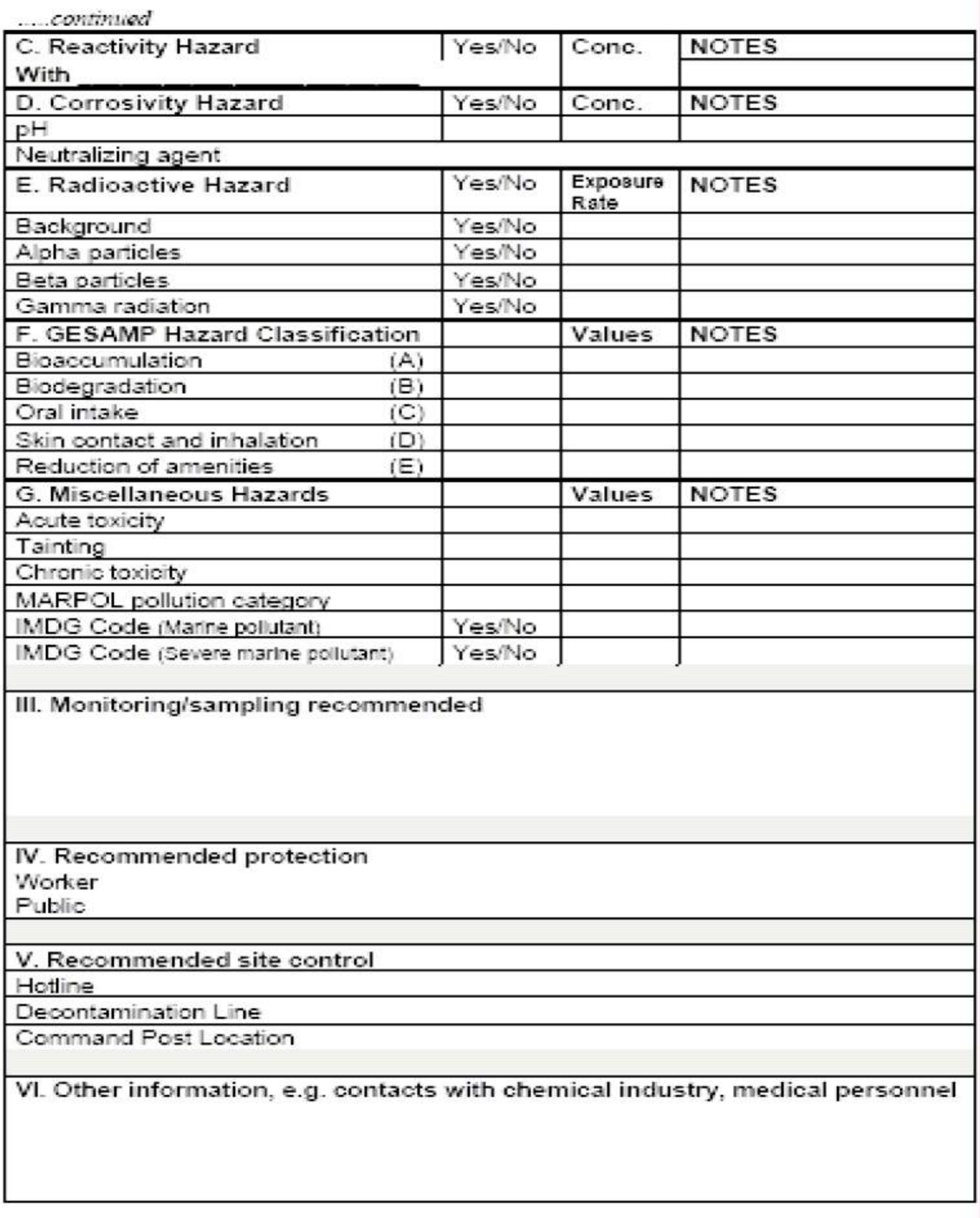

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C. Reactivity Hazard	Yes/No	Conc.	**NOTES**
With ____________			
D. Corrosivity Hazard	Yes/No	Conc.	**NOTES**
pH			
Neutralizing agent			
E. Radioactive Hazard	Yes/No	**Exposure Rate**	**NOTES**
Background	Yes/No		
Alpha particles	Yes/No		
Beta particles	Yes/No		
Gamma radiation	Yes/No		
F. GESAMP Hazard Classification		**Values**	**NOTES**
Bioaccumulation (A)			
Biodegradation (B)			
Oral intake (C)			
Skin contact and inhalation (D)			
Reduction of amenities (E)			
G. Miscellaneous Hazards		**Values**	**NOTES**
Acute toxicity			
Tainting			
Chronic toxicity			
MARPOL pollution category			
IMDG Code (Marine pollutant)	Yes/No		
IMDG Code (Severe marine pollutant)	Yes/No		
III. Monitoring/sampling recommended			
IV. Recommended protection Worker Public			
V. Recommended site control			
Hotline			
Decontamination Line			
Command Post Location			
VI. Other information, e.g. contacts with chemical industry, medical personnel			

The above mentioned information should be easily available in a handy way.

Other sources of information

One of the comprehensive sources of information for chemical spills responders is CAMEO can be used to access, store, and evaluate information critical for developing emergency plans. Over the last 15 years.

Over the past two decades, the software CAMEO suite has brought first responders from an era in which they gleaned emergency response information from maps and reference books spread out on the hoods of their trucks to a time when up-to-date, comprehensive information on chemical plumes, toxicity risks, and susceptibility of chemical mixtures to burn or explode can be displayed with a few strokes on a computer keyboard. CAMEO Chemicals is the latest addition to this innovative software line. CAMEO Chemicals is an online, easier-to-use version of the most popular components of the CAMEO program, the chemical database and the reactivity prediction tool.

CHRIS

The Chemical Hazards Response Information System. It is a free online information source developed and maintained by the US Coast Guard (CHRIS) (www.chrismanual.com). The system is designed to provide information needed for decision-making during emergencies that occur during the water transport of hazardous chemicals. CHRIS contains information for approximately 1,000 chemical products.

Transport Oriented Database on Chemical Substances **(TROCS)** was developed to assist in making decisions related to marine pollution emergencies caused by hazardous and noxious substances (HNS) and certain crude and refined oils. The database contains a number of useful case histories and can be downloaded from the web-site of the Regional Marine Emergency Pollution Centre for the Mediterranean Sea (www.rempec.org).

NOAA Reactivity Worksheet. A database of reactivity information for more than 6,000 common hazardous chemicals is produced by the National Oceanic and Atmospheric Administration. The worksheet can be downloaded from www.response.restoration.noaa.gov.

3.3. Behavior in Environment

Certain actions should be taken when accidents involving chemicals and dangerous goods occur. These actions are often the same for most types of accidents, regardless of the circumstances and materials involved. When responding to a chemical spill at sea, it is important that the measures are adjusted for the chemical's physical behavior in water. Chemicals spilt in water can evaporate rapidly when in contact with water, float on the surface, dissolve rapidly in water, or sink to bottom. A chemical spill may exhibit more than one of these properties at the same time. For example, it may float on the surface of water and at the same time evaporate and/or dissolve. It may also react with water.

3.3.1. The drift and spread of chemical spills

The drift and spread of a chemical spill in the aquatic environment (fig.3) should, as early as possible after the start of the release, be assessed or calculated so as to form the basis for a risk analysis. A simple, rough estimation is often times better than nothing. The estimation should, as far as possible, be based on the spills physical properties as well as environmental conditions like temperature, wind, water current, etc.

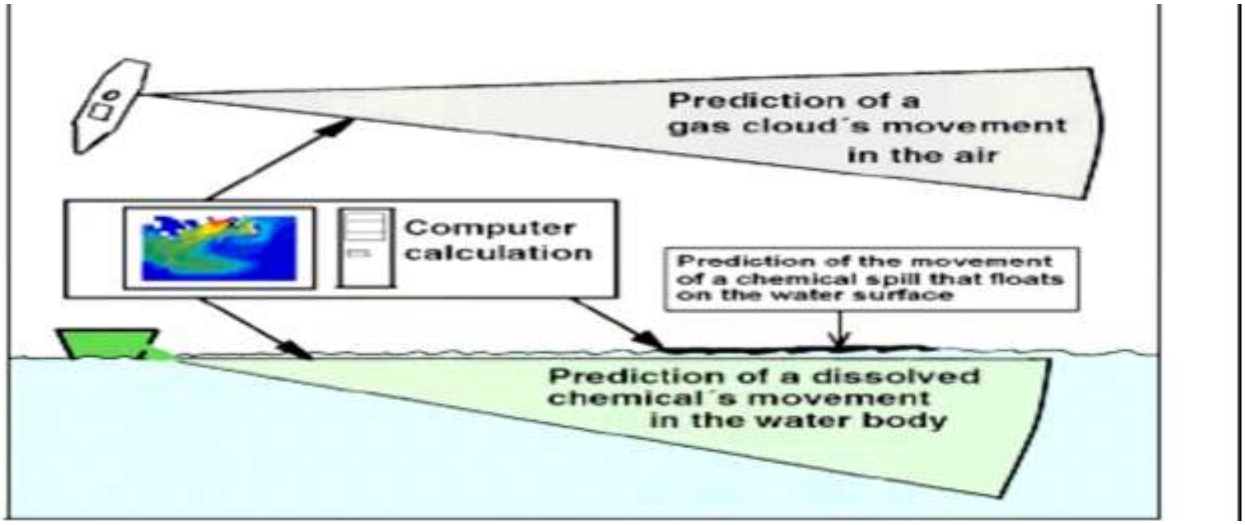


Figure 3. *The drift and spread of chemical spills can be forecasted by computer models.*

3.3.1.1. Forecasting behaviors in the air

Forecasting the spread of gas clouds in the air can be estimated very roughly for the Groups G and GD by means of Table 4. It is applicable for Groups G, GD, E, ED, FE, FED, DE (all Groups with G or E). Such estimates should always be regarded with reservations and never be alternatives for monitoring.

Table 4. Forecasting the spread of gas clouds in the air

Release	**Health Risk Fire** **Ammonia** **Venyl Chloride** **Chlorine**	**Explosion** **Methane (LNG)** **Propane (LNG)** **Butane (LPG)** **Ethylene** **Butylene- Butadiene**	**Ammonia** **Vinyl Chloride** **Methane (LNG)** **Propane (LPG)** **Butane (LPG)** **Ethylene** **Butylene- Butadiene**
Tonnes	**Meters/Nautical miles Downwind**	**Meters/Nautical miles Downwind**	**Meters/Nautical miles Downwind**
0.1	**1,000 / 0.12**	**200 / 0.12**	**200 / 0.12**
1	**2,000 / 1.24**	**400 / 0.25**	**400 / 0.25**
10	**5,000 / 3.11**	**1,000 / 0.62**	**1,000 / 0.62**
100	**10,000 / 6.21**	**2,000 / 1.24**	**2,000 / 1.24**
1,000	**20,000 / 12.43**	**4,000 / 2.49**	**4,000 / 2.49**

Note. The above Table 4 can also be applied to liquid chemicals (which are flammable and especially hazardous for health) in the Groups E, ED, FE, FED and DE. The spread of evaporated gas from spills of these chemicals can be calculated very roughly by multiplying the values in the table by VP/100. VP is the liquid's vapor pressure in kPa, which is less than 100 at ambient temperature.

It is often difficult to find time to calculate the spread of instantaneously formed gas clouds caused from accidents, even if handy computerized models were available. Sometimes, it is impossible to calculate and predict gas cloud distribution even with the aid of very sophisticated modeling tools. Certain atmospheric conditions (stratification) and/or substance properties may result in peculiar gas behavior that makes the forecasting difficult.

3.3.1.2. Floating Spills

It is rather easy to forecast a behavior of a chemical spill that floats on the water surface by using the model applicable from the oil spill response practice. The spill's fate is influenced by the following processes:

a) The drift on the surface
b) The spread on the surface
c) Evaporation
d) Dissolution and dispersion
e) Chemical reactions and other conversion processes

Various models have been developed, that are applicable for modeling of oil drift, but very few have been validated against chemical spills, especially in real operational conditions at sea.

Simple forecasting models have been developed for chemical spills that float on the water surface. For the sake of simplicity, the spills are supposed to neither evaporate nor dissolve. This principle can also be used for manual calculations and is briefly described below.

This type of calculation is applicable for Groups FE, FED, F and FD (all Groups with F). Figure 4 shows how a floating chemical slick's drift can be calculated by means of a vector diagram in the same way as oil spills. However, most chemical spills belonging to the above mentioned Groups, except for F, will disappear by evaporation and/or dissolution within roughly 10 hours.

3.3.1.3. Dissolved spills in the water body

The method shown below is applicable to the Group D only. If the current of the water is slow, even the dispersion can be roughly calculated according to Figure 5 and Table 5. This method cannot be applied for stagnant (or almost stagnant water) or for chemicals whose density differs too much from that of the water. This method also cannot be used for turbulent water.

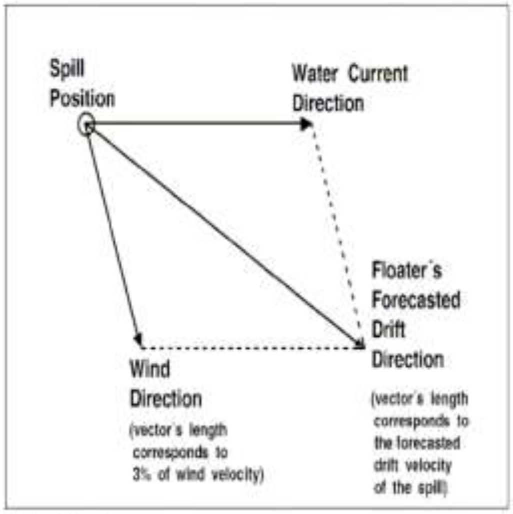


Figure 2 - 4

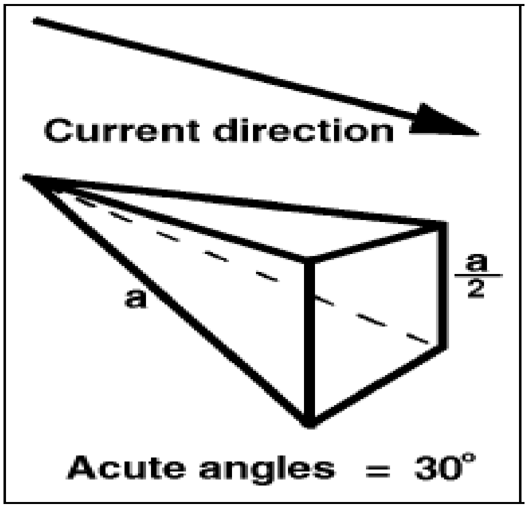


Figure 2 - 5

Figure 4. *Forecasting the spread on water surface.* **Figure 5.** *Forecasting the dispersion in water body.*

It is assumed that the soluble chemicals that spread to water column by the way of currents form a pyramid with 300 angles. In such a condition, the concentration of chemical can be determined based on Table 5.

Table 5. *Concentration of chemicals in water*

	Concentration 1 g/m3		Concentration 1 g/m3	
Release Tonnes	A metres	Nautical Miles	A metres	Nautical Miles
1	500	0.3	5,000	3
10	1,000	0.5	10,000	5
100	2,000	1	20,000	11
1,000	4,000	2	40,000	22

3.3.1.4. Sinking Chemical Spills

It is very difficult to calculate the fate of a spill that sinks to the bottom. The reason for this is the number of parameters that influence the process (Figure 6). Chemical's density affects the velocity by which the chemical sinks to the bottom. Its surface tension and solubility (even if very low) influence its behavior on the water surface as well as its dispersion and spread in the water column, during its sinking. The water current, together with the water depth and the chemical's density, have a decisive factor in how long a distance the chemical will move in the current's direction before it reaches the bottom. Chemical's duration on the bottom is, among other factors, dependant on its solubility. If the solubility is e.g. 1% or 0.001%, it must obviously have a pronounced effect on its duration on the seabed. Also, the existence of water currents close to the bottom influence the duration. Chemical may also penetrate into the bottom sediment. The degree of penetration depends on the sediment's properties and structure.

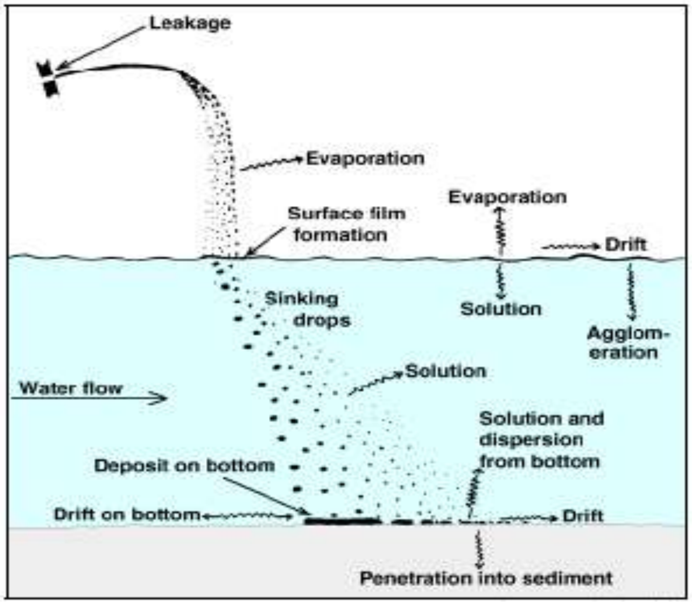


Figure 6. *A sinking chemical and its behaviors*

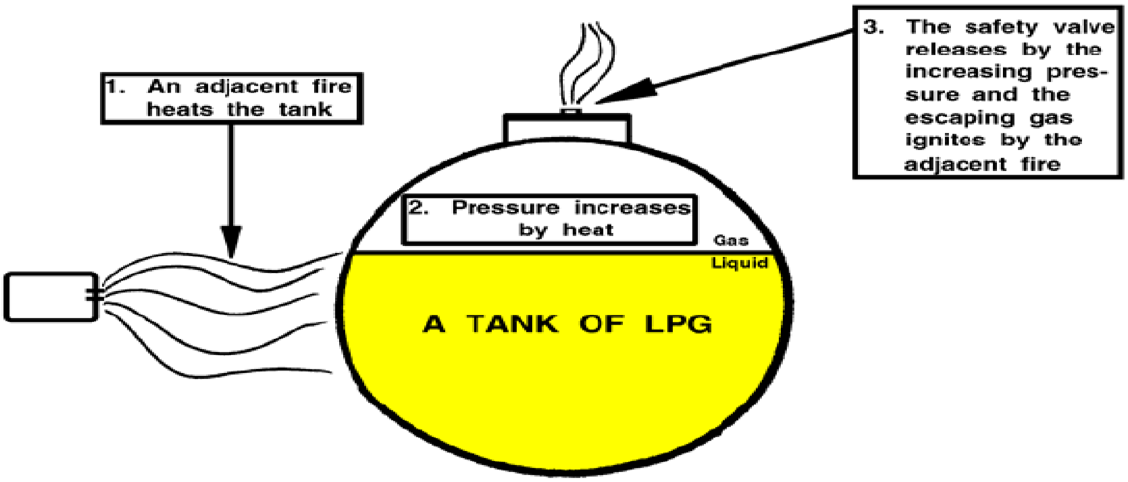


Figure 7. *How a BLEVE could be initiated*

3.3.1.5. Boiling Liquid Expanding Vapor Explosion (BLEVE)

BLEVE is an important concept in the field of emergency response, especially in accidents involving LPG (liquefied petroleum gas). Many disastrous accidents have occurred when LPG tanks have exploded in BLEVE. Also, other substances other than LPG may be involved in BLEVE accidents. BLEVE may occur when a pressurized tank, containing e.g. LPG, is exposed to an external fire. If the tank cannot resist the increasing pressure, it will burst and the LPG content will be thrown around, mix with air, and ignite a storm of fire.

Explosion is accompanied by a strong pressure wave and a gigantic fireball from a large tank that might even been mistaken for a nuclear explosion. A very violent outer fire is one possible cause for a tank to burst. In such a case, the capability of the safety valve may not be enough to keep the pressure down. Another reason for the cause is the weakening of the tank's wall caused by corrosion, mechanical damage, etc. (Figure 7)

BLEVE may occur in similar situations on board ships. A response option for such an occasion is to douse it with water from a safe distance. But evacuation should also be considered.

3.3.2. Models for forecasting behavior of HNS

Various computer models exist by which an operator, after some education and training, can forecast the fate of the spill's future. However, on the spot of incident, it should be emphasized that the forecast's reliability depends fully on:

1) The model's construction, validity, and accessibility,
2) Integrity of the all inputted data.
3) Level of professionally when the model is run.

Many computer models have wide limitations. It is common that for gas cloud models, one cannot consider the structure of the ground or water surface (e.g. flat country, forest, calm water, rough sea). Some models cannot even consider mountains as obstacles in a cloud drift. Some drift models are not able to account for the chemical's physical properties (e.g. water solubility) which give a misleading or erroneous picture of their drift. The initial forecasting can be made using very easy assessment model given below. Examples are given below of short description of programs, which can be used for predicting behavior of spilt HNS in the atmosphere and at sea.

3.3.2.1. Gas Clouds in Air

NOAA has developed and launched on the INTERNET a program which allows forecasting behaviors of toxic gas clouds in the air (Figure 8). **ALOHA** (Areal Locations of Hazardous Atmospheres) is a modeling program that estimates threat zones associated with hazardous chemical releases, including toxic gas clouds, fires, and explosions. (www.response.restoration.noaa.gov/cameo/aloha.html, Threat zone is area where a hazard (such as toxicity, flammability, thermal radiation, or damaging overpressure) has exceeded a user-specified **Level of Concern (LOC)**.

ALOHA takes into consideration the following factors:
Wind Speed & Direction, Ground Roughness, Cloud Cover, Air Temperature, Atmospheric Stability, Inversions, Relative Humidity, Pressure, & Volume, Container / conveyance, Type of release, Physical state of chemical.

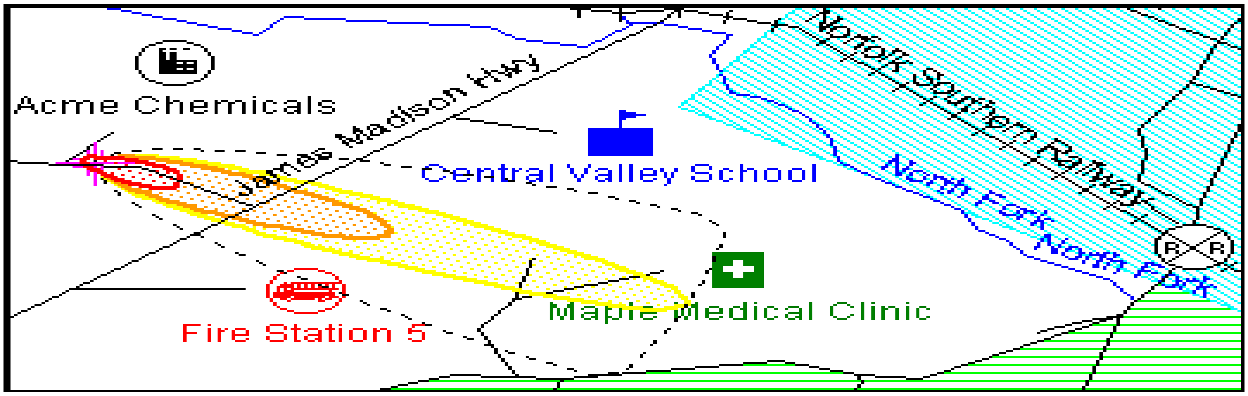


Figure 8. *An ALOHA threat zone plot displayed on a MARPLOT map. (Source* ***NOAA)****The red, orange, and yellow zones indicate areas where specific Level of Concern thresholds were exceeded.*

Key Program Features

- Generates a variety of scenario-specific output such as threat zone plots, threat at specific locations, and source strength graphs.

- Calculates the rate of release for chemicals escaping from tanks, puddles (on both land and water), and gas pipelines, and predicts how that release rate changes over time.
- Model release scenarios: toxic gas clouds, BLEVEs (Boiling Liquid Expanding Vapor Explosions), jet fires, vapor cloud explosions, and pool fires.
- Evaluates different types of hazards (depending on the release scenario) such as toxicity, flammability, thermal radiation, and overpressure.
- Displays threat zones on MARPLOT maps (and on ArcView and ArcMap with the Arc Tool extensions)
- Works seamlessly with companion programs like CAMEO and MARPLOT. It can also be used as a standalone program.

ALOHA was developed jointly by NOAA and the Environmental Protection Agency (EPA), and it runs on both Macintosh and Windows computers.

MET (Modells für **E**ffekte mit **T**oxischen Gasen**)** (www.memplex.com) makes a dose-effect-coupling for effects from toxic gases, and it also estimates risks of human injuries in an area of the wind downward direction of the accidental release.

MET consists of the following four main modules:

1. The instantaneous release of toxic substances as a puff and the formation of a gas/air cloud mixture.
2. The dispersion of the toxic gases and calculation of the concentrations as a function of the distance (half sphere box model).
3. The transformation into doses.
4. The dose/effect-coupling based on a modified pharmacological receptor theory that was developed to evaluate the health impact.

The input values MET needs:

1) Escaped substance weight.

2) Wind speed.

3) Threshold value for the substance.

Other parameters are automatically provided by the system so that hazardous distances could be calculated.

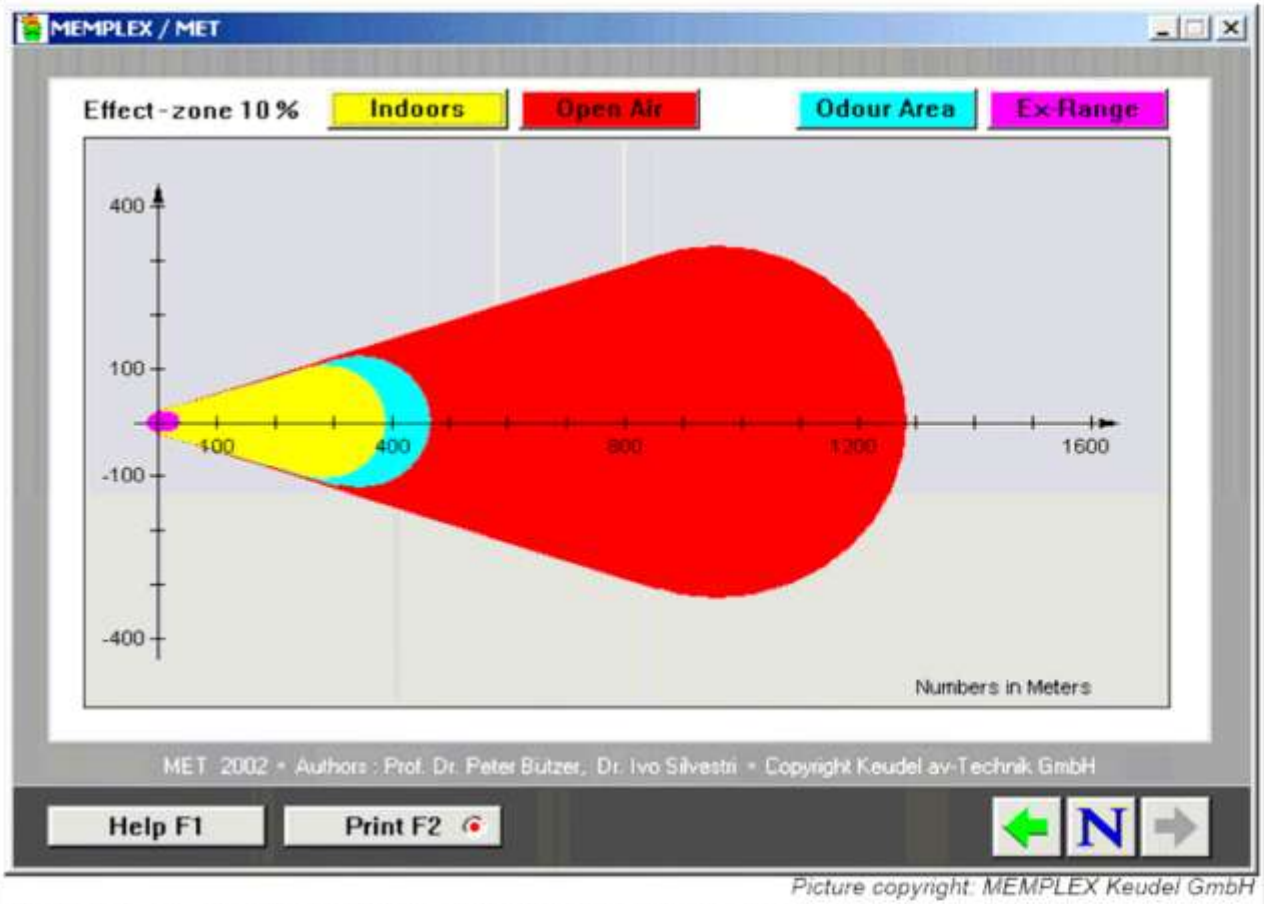
MET has modules for the following simulations.

1) The washout effect of the cloud by rain.

2) Influence of a simultaneous fire.

3) Dispersion characteristics of heavy gases.

The model is stable, even for large variations of toxic values, as it can integrate several different values. In addition, the lower explosion limit is used to calculate the size of the explosive mixture of a substance and air. Effects on mixtures of substances from fires can also be calculated.



Picture copyright: MEMPLEX Keudel GmbH

Figure 2 - 9 Graphical MET description of a gas cloud dispersion in air.

Figure 9. *Gas cloud dispersion in the atmosphere.*

3.3.2.2. HNS in Water Column

CHEMMAP is a three dimensional chemical discharge model designed to predict the trajectory, fate, impacts, and biological effects of a wide variety of chemical substances. It was developed by Applied Science Associates, Inc. (ASA), USA (http://www.asascience.com or www.appsci.com).

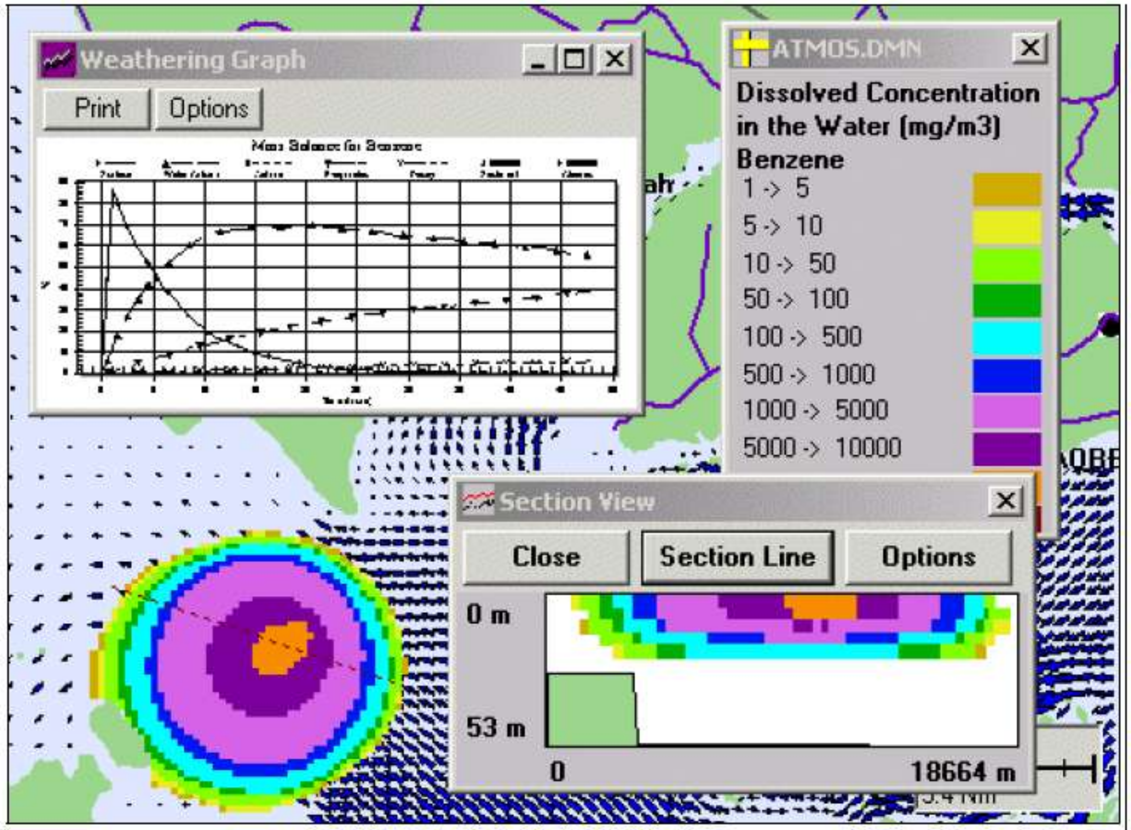


Figure 2 - 11

Picture source: Applied Science Associates, Inc.

Figure 10. *Example of submission of results of modeling by CHEMMAP*

Applications for CHEMMAP includes:

- Hind cast/forecast of spill response.
- Natural resource damage assessment.
- Contingency planning - including worst- case scenario.
- Evaluation of point source discharges.
- Cost-benefit analysis.
- Drills and education.

Features of CHEMMAP

- Contains ASA's own GIS and can be used in other GIS software such as ArcView®.
- Location of specific environmental/ biological data applied to any fresh or salt aquatic environment in the world.
- Suitable for using a variety of hydrodynamic file formats.
- Easily interpreting visual displays of concentrations over time.
- 3D Viewer capabilities.
- Biological exposure model that predicts exposed fish and wildlife impacts.
- MSDS database linked to the physical- chemical database.
- Extensive chemical database providing physical- chemical data.

CHEMMAP simulates the following processes:

- Initial plume dynamics.
- Slick spreading, transport, and entrainment of floating materials.
- Evaporation and volatilization (to atmosphere).
- Transport and dispersion of dissolved and particulate materials in the water column and in the atmosphere.
- Dissolution and adsorption of suspended sediments.
- Sedimentation and resuspension.
- Natural degradation.
- Shoreline entrainment.
- Boom effectiveness.

SPILMOD was developed in Russia.

It can be used for calculating the drift and spread of chemical spills in aquatic environment.

The model takes the following factors into account:

- Spill volume and concentration
- Water currents
- Sinking, dispersion, and evaporation

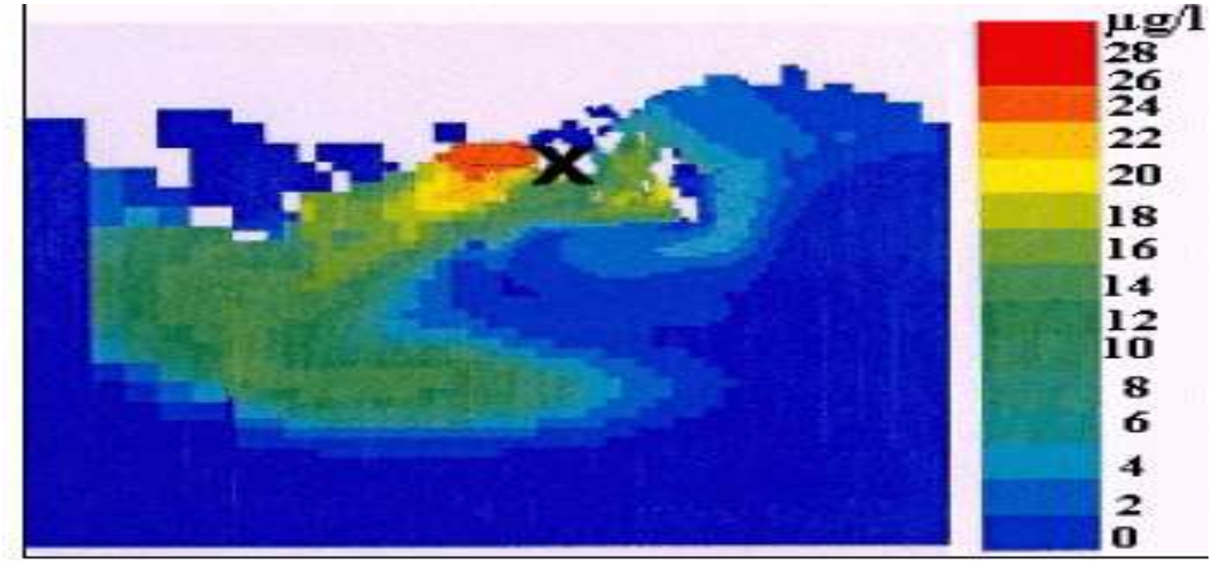


Figure 11. *Example of distribution of spilt chemicals in water column.*

3.4. Impact of Spill

Once the dimensions and/or concentrations of a spill are known, the impact of the spill can be assessed. For these purposes, national methods and legislation should be used.

The sensitivity of the area between the initial spill and its final destination determines the seriousness of a spill. Risk assessment must incorporate the evaluation of the threat posed by the released chemical to human health, the marine environment, and related interests. Theoretical approach to determining the impact can be done with the help of computer model predictions.

Measurements from the scene will determine the actual situation. Assessment of risk for fire, explosion, leakage, as well as its impact on health and adjacent areas can lead to the establishment of restriction areas (risk zones). These decisions are based on results from information and behavior of spilt HNS. Knowledge of this information is critical for responders.

Chapter 4.

Monitoring

4.1. Gas monitoring by portable instruments

In chemical accidents it is crucial to monitor the air for concentrations of hazardous substances. The purpose of gas monitoring is to assess both toxic and fire/explosion hazards, as well as to map the area where unprotected personnel should be evacuated, and to judge the appropriate level of body protection for response personnel. In certain situations, the read- out values can be used directly for designing risk areas. In other circumstances, instruments can be used to check the risk areas that are already assessed or defined, according to some calculation method or forecasting model.

The most difficult measuring task on a chemical accident site is to make rapid identification of unknown airborne substances with portable instruments. Such work requires sophisticated instruments and trained expertise that is not often available when the first risk assessment is going to be made. Proper use of portable gas monitoring instruments generally requires exact identity of the gas. Luckily, this is often the case, especially when a single chemical substance is involved. Its identity is often known to the responders.

4.1.1. Monitoring instruments

In a world market, there are hundreds of manufacturers offering thousands of different models of hand-held, portable, transportable, and mobile gas detection and monitoring instruments that can be used in chemical accidents for risk assessment and evaluation. This should be used according to manufacturer’s instruction.

4.1.2. Gas tracing

The main objectives of gas tracing, in case of a chemical accident, are to find dangerous toxic gas contaminated areas and assess reasonably safe outer limits for unprotected personnel. This type of instruments must be able to detect very low concentrations of hazardous gases (ppm-levels). List of various hand-held or mobile trace gas detection and monitoring devices:

- Gas detection tubes
- IR trace gas detectors
- Semiconductor instruments
- Portable gas chromatographs
- Photoionization instruments
- Mobile mass spectrometers

Gas detector tubes, semiconductor instruments, and some photoionization instruments are relatively simple hand- held devices. Note that these instruments cannot be used for accurate readings. The results are approximate. Portable gas chromatographs and mobile mass spectrometers are examples of more sophisticated instruments. These instruments are miniaturized and automated laboratory equipment. They generally give accurate readings but require skilled personnel to handle.

Monitoring should be performed by a personnel equipped with breathing apparatus, trained in monitoring instruments, and familiar with their function. The measurements should be carried out from outside (gas-free area) towards inwards to the dangerous area. The position, where the first recording is noticed, is on the fringe of the evacuation area. By doing further monitoring around the place of the accident, a map of the evacuation area can be drawn.

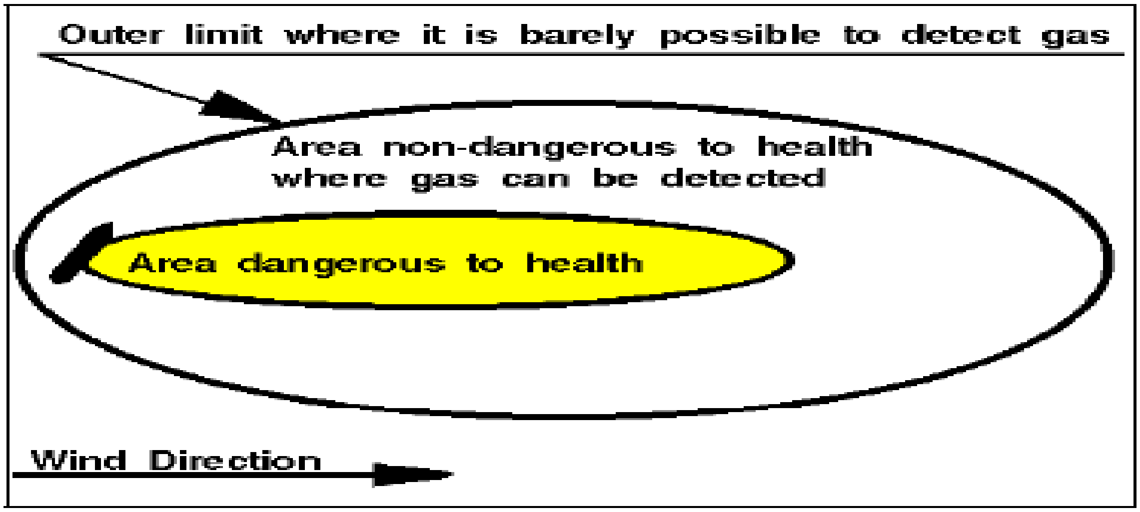


Figure 12. *The outer limit of measurable concentrations and the area of gas concentrations which are dangerous to health.*

However, it should be emphasized that a gas cloud, in reality, often doesn’t give uniform and smooth curves as shown in Figure 12. The boundary line, however, should be leveled along the outermost gas registrations. Gas clouds often move irregularly due to air turbulence and other environmental conditions.

If no monitoring device is available, a safe evacuation area must be established around the scene of the accident with a great margin for safety until more information support a change in judgment.

4.1.3. Flammability Risk Monitoring

Personnel who are using instruments to assess flammability/explosive risks should fully understand the meaning of the concepts LEL/LFL and UEL/UFL(Annex A). The objective of flammability (or explosive) risk monitoring is to assess the outer limits of a flammable gas in the contaminated area. gas monitoring of oluene could be taken as an example of a safe toluene concentration regarding flammability risk is 1,000 ppm (which is 10% of the Lower Explosive Limit for toluene), while a safe health risk value for toluene regarding inhalation is only a few ppm, which can only be measured with trace gas detectors.

4.1.4. Oxygen-Deficient Air Monitoring

The oxygen level in confined spaces, such as cargo holds or tanks, can decrease because of work being done such as welding, cutting, or brazing. It can also be decreased by oxygen- consuming reactions (metal rusting or cargo oxidation) or through microbial action (fermentation). The oxygen concentration also decreases if air is displaced by another gas such as inert gas, carbon dioxide, nitrogen, and hydrocarbons. If such gas causes total displacement of oxygen, an unprotected person will rapidly become unconscious and die.

Oxygen-deficient means that there is not enough oxygen in the space to safety breathe. **Normal fresh air contains 20.8 percent oxygen compared to less than 19.5 percent in an oxygen-deficient atmosphere**. **Air that has less than 10 percent oxygen can rapidly cause unconsciousness, and levels below 8 percent can quickly cause death**. The objective of oxygen-deficient air monitoring instruments is to assess the outer limits of an oxygen deficient area where it is reasonably safe for unprotected personnel (Oxygen concentration above 19.5%).

Any atmosphere with less than 19.5% oxygen should not be entered without any approved self-contained breathing apparatus (SCBA).

4.1.5. Monitoring the water column

Monitoring the dispersion of chemical spills in the body of water is often performed by taking water samples with hand-held devices at various positions and analyzing the samples for the actual chemical. Sometimes, the analyses can be done by portable equipment, but on many occasions the samples must be brought to stationary laboratories. Well-equipped portable laboratories exist, which can be placed close to the site of the accident.

Monitoring can be achieved in some systems by probes containing parts of the analytical equipment which can perform analyses automatically. The probe is manually submerged or towed. Selection of measurement principle and monitoring equipment is depended upon the type of spilled chemical. (Figure13)

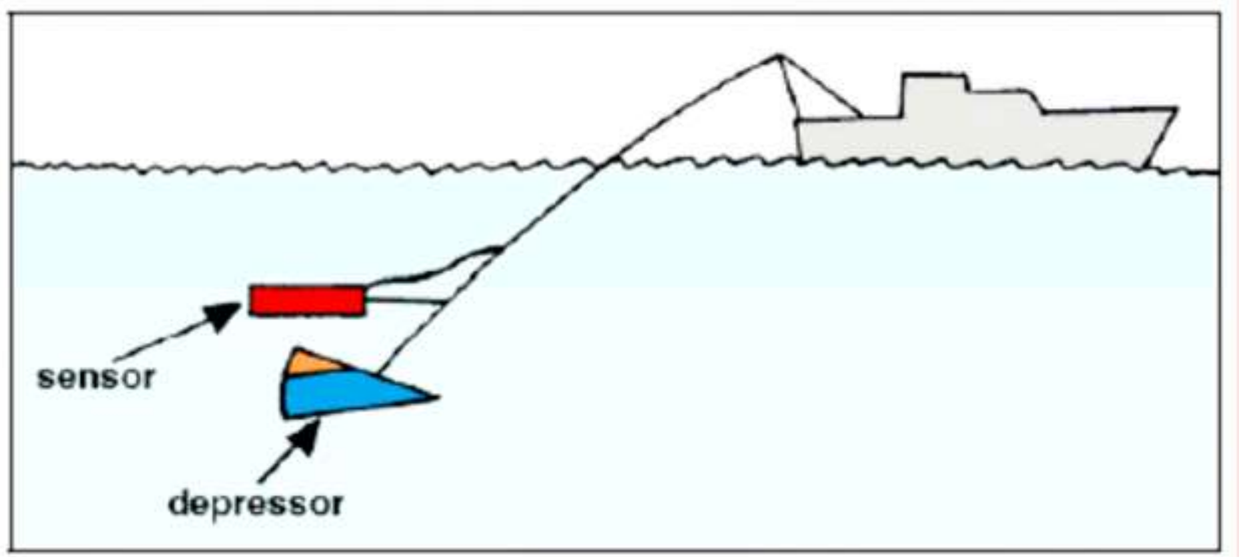


Figure 13. *Monitoring the body of water with a towed probe.*

The physical principle of measurement may be, for instance, pH, light absorption, electrical conductivity, or turbidity. Low concentrations of many organic substances (e.g. hydrocarbons or halogenated hydrocarbons) may be very difficult to measure with portable equipment. However, in recent years, different types of active sophisticated equipment have been developed that are capable of monitoring such substances in low concentrations. Such monitoring must often be carried out by specialized experienced personnel.

4.1.6. Monitoring surface spills

It is well known that oil spills on the water surface can be detected and monitored by means of various types of airborne remote sensing instruments.

Oils spills are often viscous and form relatively thick (> 1 mm) layers that change physical properties of the water surface, allowing them to be monitored by remote sensing techniques. But, on some occasions, even very thin oil films (< 0.1 mm) can be caught by certain instruments. Floating chemical spills also often form such thin films at the surface. Such thin films dampen the sea surface's capillary waves, thus reducing the intensity of the backscatter caused by the Side-Looking Airborne Radar (SLAR). The smooth area of the surface slick will, therefore, appear as a relatively dark area in the SLAR image. The slick could also change the UV reflectivity of the surface and be seen by an UV scanner. It could also change the surface's radiation temperature allowing to be registered by IR instruments like an IR scanner and a Forward-Looking Infrared Imager or FLIR.

4.1.7. Monitoring sunken substances on the seabed

A chemical spill that sinks to the bottom after an accident will scatter at the bottom area. Scattered spills, on the seabed, may be difficult to monitor. Yet, it is important to map the spill in order to guide the responders. The chemical at the bottom is always slightly soluble in water, though the solubility sometimes is very low. The solubility must be checked and the concentrations, in the adjacent water, must be monitored in order to evaluate the risks for environment, fishery, recreation, fresh water intakes, etc. A liquid pool, on the bottom, has a phase boundary surface which can be recorded by an echo-bounder

Chapter 5.

Sampling

Sampling and subsequent analysis will answer the questions regarding spills’ origin as well as their properties and effects. To accomplish this, samples should be taken for several different purposes. Some spills might involve contacts and co-ordination with other countries regarding sampling and analysis. Occasionally, foreign agencies should be contacted to exchange samples, analysis results, examination reports, etc. The following list describes eight purposes of sampling after incidents or accidents involving hazardous substances. Most often, only a few of them are necessary in a specific case.

5.1. Occupational safety

When necessary, the spill should be examined (analyzed) to establish whether there are health risks for the response personnel. The substance might be flammable and could cause fire and/or explosion. It may also be toxic and cause illness if inhaled or exposed to skin.

5.2. Penal liability

The responsible polluter should, if possible, be identified and be charged for the spilling. This can be done by comparing chemical analyses of samples from the spill with samples from the suspected sources. If identity is established between the spill and a suspected source, this can help to identify the polluter.

5.3. Polluter’s economical liability

The results of sampling have often been used as a basis for compensation claims against the polluter. These claims are comprised of costs associated with response and cleanup measures, or damage to property, fishery, recreational areas, etc. Above all, it is important to tie the suspected polluter to the damage, in order to confirm the claims. Sampling procedures, which are connected to liability investigations, must be performed with great care and accuracy concerning spills as well as suspected sources. Every action should be taken to prevent a decrease in the samples’ value as evidence.

5.4. Spill response planning

On some occasions, special analyses can give important information, which can support the planning of response and cleanup work. It is important to study chemical and physical property data of the substance when selecting equipments and methods, as well as safety routines for the response operation.

5.5. Short term environmental protection

The substance’s acute deleterious effects on the environment are vary considerably depending on its properties. Many chemicals show acute toxic effects to the marine life and some substances have a tendency to smear beaches, plants and animals. Besides identifying the substance, it is also necessary to sample and analyze the water column, sediment, organisms, etc.

5.6. Long term environmental protection

Certain substances might cause long term deleterious effects on the environment, and some species may be knocked out, or the environment be polluted for a long time. Assessment should be done to judge how the environment will be restored. It is necessary to sample and analyze the substance itself, as well as the water, sediment, organisms, etc.

5.7. Information service

Sometimes, tricky questions are asked about the substance’s properties and effects, especially when facing a large or hazardous spillage. In such cases, it is important to give rapid and correct information in order to reduce anxiousness and circulating of rumors. Sampling and analysis can thereby provide the basis for information to be given and be an information channels.

When informing the public and those who are directly affected by the spill, it is important to account for certain data. For example:

- The origin and extension of spill
- The properties of spilled substance and its spread in the environment
- Effects on human and environment

- Consequences for various parties and bodies
- Ongoing work regarding response, cleanup, and disposal Sampling

5.8. Disposal

Selection of techniques for the subsequent disposal is based on the type of spilled substance, its properties, and the volume of spill. Many disposal plants are specialized for certain hazardous materials and cannot process other types.

General checklist for sampling

1. Sampling of unknown materials should be conducted on a "worst possible case scenario." For example, if nothing is known about the substance, it should be considered as extremely hazardous and sufficient safety precautions should be taken.

2. All spills encountered and all potential sources of spills should be sampled. It is important to samples from both spill and the source, even on occasions where it may seem quite clear where the spill originated. Examples of the type of sampling equipment, and sampling procedures and routines can be found in HELCOM Manual.

3. Even if a spill has scattered on the water surface and only thin sheens remain, every possible effort should be made to take at least a small sample. No sample volume is too small to be shipped to the laboratory.

The laboratory can often analyze very small samples such as water samples that seemingly consist of pure water, or sample pads that do not show any trace of substance.

4. Assistance should be received from appropriate experts on occasions of uncertainties. All sampling of chemicals on board vessels or in other sources should be left to the crew or staff (if possible), or should be carried out in close co- operation with the crew/staff. Special safety precautions must be taken during sampling activities in atmospheres that might be explosive.

5. Samples and sampling equipment should be handled and stored so that the samples cannot be manipulated and mixed up so that it will not be contaminated by strange substances. Samples should be handled as legal evidence and should be kept in a "chain of custody" until identification and possible legal procedure has been completed. Therefore, always use a sealable and individually numbered safety bags.

6. A bottle containing a sample should not be placed in the sampling kit together with the clean equipment. Reusable sampling equipment should be always very carefully cleaned, and put into clean plastic bags, before restoring it in the sampling kit case. Used sample bottles must not be used again, not even after careful washing.

7. Make note of all relevant information about samples and sample sites. Use a miniature camera or a video camera to record observations, which are considered important for the investigation.

8. The samples should be immediately sent to the Sample Coordinator. Quick handling of samples is important. If the transmittal is delayed, the samples should be kept under a temperature less than +4°C.

9. Consumed equipment should be replaced as soon as possible so that the sampling kit case will always be fit for use, so that new samples can always be quickly taken, packed, and sent away.

Handling of spill information

The whole chain of activities leads to information that will be presented about the spill. This chain consists of:

- Sampling
- Sample keeping and transmittal
- Identification, labeling, documentation
- Chemical, physical and biological analyses
- Judgment of the analysis results
- Presentation of the analysis results

Each step must be taken with care and accuracy. This is a prerequisite for compilation of an information report, which is only as good as what the circumstances allow. Points to be observed during sampling and subsequent handling of samples are:

- Several samples must be taken from spills, covering large areas or divided areas in several locations.

Sampling

- Sampling in a suspected source must be performed in such a careful way that the suspected polluter with certainty can be tied to, or cleared of, the spill.
- All samples must be labeled so that they can be unmistakably referred to the sampling points.

● Sample containers must be labeled, sealed, and kept in such a way that any supposition on confusion or manipulation can be excluded.

● All sampling documentation, as well as other evidence, must be available during the investigation, but also be protected from loss, confusion, and manipulation.

● Continuous record-keeping must be made regarding all transmissions of samples, and other evidence and documentation between officials. The Sample Coordinator is responsible for transmission of samples to the appointed laboratories.

Advice and directions for safety routines

Directions must be acquired from the ship's officers regarding how sampling should be performed, considering the current safety regulations on board the ship. Sampling in tanks and spaces, within the ship’s Hazardous Areas, should be carried out by the ship’s own crew. If a ship has a sampling equipment of its own, this should be used first. The sampling should be performed under the supervision of the personnel which is responsible for the sampling. If this is not possible, sampling should only be performed with external equipment, after the approval by the ship’s officers or the ship’s surveyor.

When samples are taken in tanks containing volatile noxious, the following advice shall be observed:

● Level A protection shall be used

● Only one hatch at a time should be opened.

● One person should perform the sampling and another should supervise the sampler (safety guard). The latter shall observe the sampler’s condition and see to it that he or she is taken away to a safe place if encountered by noxious gases (intoxication symptoms).

● Only explosion proof equipment (EEx-marked) should be used.

● The sampler must not have loose items in the pockets. They might fall down into the tank.

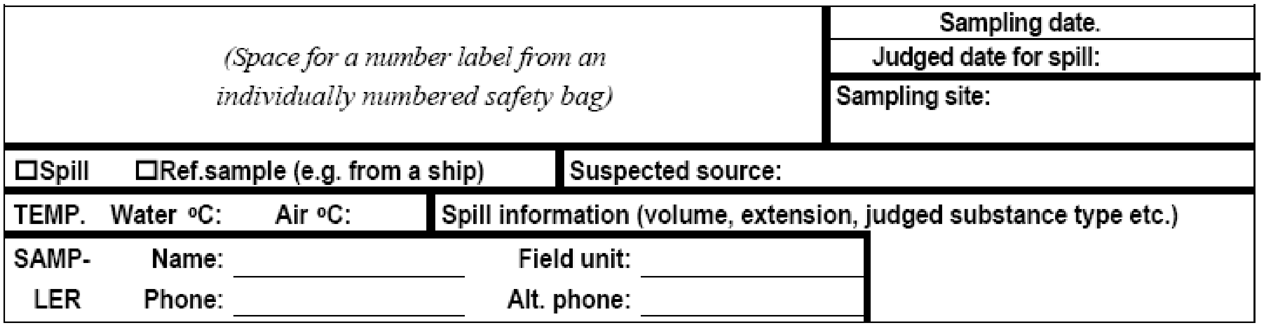
During loading, equipment made of metal for sampling and ullage-sounding, must not be brought into the tank, or be left in the tank, within 30 minutes after loading has stopped. Examples of such equipments are steel measuring tapes and steel measuring sticks. Non-conducting equipment, without metal parts, may be generally used at any time. Cords, however, used for lowering equipment into tanks must be made of natural fibers (not synthetic materials).

After loading, equipment made of metal for sampling and ullage-sounding can be used 30 minutes after loading has stopped. However, it is important to make sure that the equipment is firmly grounded to the ship's hull before it is brought into the tank. The equipment must remain grounded until it has been removed from the tank.

Sample custody and documentation

Samples and sampling equipment should be handled and stored so that samples cannot be manipulated, mixed up, or be contaminated by strange substances. Samples should be handled as legal evidence and be kept in a "Chain of Custody" until identification and possible legal procedure have been completed. Such a Chain of Custody should be maintained by means of durable (approved), sealable, and individually numbered safety bags. Three detachable adhesive number labels, with identical numbers, should be on the bag. Different safety bag number must be assigned to each sample. The number is the identification of the sample. One of the detachable number labels (table 6), shall be affixed onto the glass sample bottle label. The next number label shall be placed on the outer plastic jar, and the third label on the Letter of Request. A sample label should be affixed to each sample bottle.

Table 6. *Sample label*



(Space for a number label from an individually numbered safety bag)

Sampling date.

Judged date for spill:

Sampling site:

☐Spill ☐Ref.sample (e.g. from a ship)

Suspected source:

TEMP. Water °C: Air °C:

Spill information (volume, extension, judged substance type etc.)

SAMP-LER Name: __________ **Field unit:** __________

Phone: __________ **Alt. phone:** __________

The following documentation is important when samples are taken and shipped.

A Letter of Request with a specification and information on the enclosed samples. Necessary information, in the Letter of Request and/or in the sample bottle label, is as follows:

- District, sampler, unit
- Date and position (or sampling site on board the vessel) of sampling

- Spill’s volume/appearance and substance type suspected source

Shipping of samples

The Sample Coordinator collects all samples and fills in a Letter of Request, which is sent to the laboratory together with the samples. The Sample Coordinator should also call in an expert, if needed, from external institutes or laboratories to assist the sampling activities. Samples of some chemicals are to be considered as dangerous goods when they are shipped. However, if contained and packaged as described above, they can often be shipped as “limited quantities,” which means a simpler shipping requirements compared to dangerous goods. IMDG Code rules and local regulations should always be followed.

Chapter 6.

Body protection

When response activities are to be conducted where atmospheric contamination is known or suspected to exist, personal protective equipment must be worn.

Personal protective equipment is designed to prevent/reduce skin and eye infection as well as inhalation or ingestion of the chemical substance. Protective equipments for the body against contact with known or anticipated chemical hazards are divided into four categories Level A – D. These levels are briefly indicated in Table 7 below.

Table 7. *Categories of Level*

Level A

Level A protection should be worn when the highest level of respiratory, skin, eye, and mucous membrane protection is needed.

Personal Protective Equipment

- Positive pressure (pressure demand), self contained breathing apparatus, or positive pressure supplied air respirator with escape SCBA.
- Fully encapsulating chemical protective suit.
- Chemical resistant inner gloves.
- Chemical resistant outer gloves.
- Boots, chemical resistant, steel toe and shank (depending on suit boot construction, worn over or beneath suit boot).
- Cotton underwear (long- john type).*

Body protection

- Hard hat (beneath the suit).*
- Coveralls (beneath the suit).*
- Two-way radio communications (intrinsically safe/non- sparking).*

** Optional*

Level A protection should always be used if the airborne substances are unidentified. The type of environment and the overall level of protection should be evaluated periodically during the operation as you gather more information about the hazards.

Level B

Level B protection should be selected when the highest level of respiratory protection is needed. Personnel under Level B are easier to secure with rescue lines. Level B protection is the minimum level recommended for the initial site entries. This can change as more hazards are further identified and defined with monitoring, sampling, and other reliable methods of analysis. These findings are utilized with corresponding equipments.

Personal Protective Equipment

- Positive-pressure (pressure-demand), self-contained breathing apparatus, or positive pressure supplied air respirator with escape SCBA. The breathing apparatus is worn outside the suit (which is the main difference from Level A).
- Chemical resistant suit.
- Chemical resistant outer gloves.
- Chemical resistant inner gloves.
- Chemical resistant outer boots with steel toe and shank.
- Chemical resistant disposable boot covers.*
- Two-way radio communications (intrinsically safe, non-sparking).*
- Hard hat.*
- Face shield.*

** Optional*

Level C

Level C protection should be selected when the type of airborne substance is known, concentration measured, criteria for using air-purifying respirators met, and skin and eye exposure is unlikely. Periodic monitoring of the air is a must.

Personal Protective Equipment

- Full-face mask, air-purifying respirator.

- Chemical resistant clothing (one piece coverall, hooded two piece chemical splash suit, chemical resistant hood and apron, disposable chemical resistant coveralls.)
- Chemical resistant outer gloves.
- Chemical resistant inner gloves.
- Chemical resistant boots with steel toe and shank,
- Chemical resistant boot-covers,*
- Cloth coveralls (inside chemical protective clothing).*
- Two-way radio communications (intrinsically safe, non-sparking).*
- Hard hat. *
- Escape mask. *
- Face shield.*

** Optional*

Level D

Level D is primarily a work uniform and is used for nuisance contamination only. It only requires coveralls and safety shoes/boots. Other PPE is based on the situation (types of gloves, etc.). It should not be worn on sites where respiratory or skin hazards exist. The type of environment and the overall level of protection should be evaluated periodically as more information about the site are gathered and as workers are required to perform different tasks.

Level upgrading or downgrading

Reasons to upgrade to a higher level (D is lowest, A is highest):

- Known or suspected presence of dermal hazards
- Occurrence or likely occurrence of gas or vapor emission
- Change in work task that will increase contact or potential contact with hazardous materials
- Request of the individual performing the task

Reasons to downgrade:

- New information indicating that the situation is less hazardous than was originally thought
- Change in site conditions that decreases the hazard
- Change in work task that will reduce chance of contact with hazardous materials

Chapter 7.

Selection of response measures

7.1. Decision making

The selection of the response methods is highly dependent on the nature of the spill, the local circumstances, weather conditions, availability of and accessibility to equipment, and the properties of the pollutant. In addition to the criteria mentioned, political considerations would also play a prominent part in decision-making. Sometimes it is difficult to assess which response technique is most suitable for the spill concerned. Table 8 gives some recommendations on this problem.

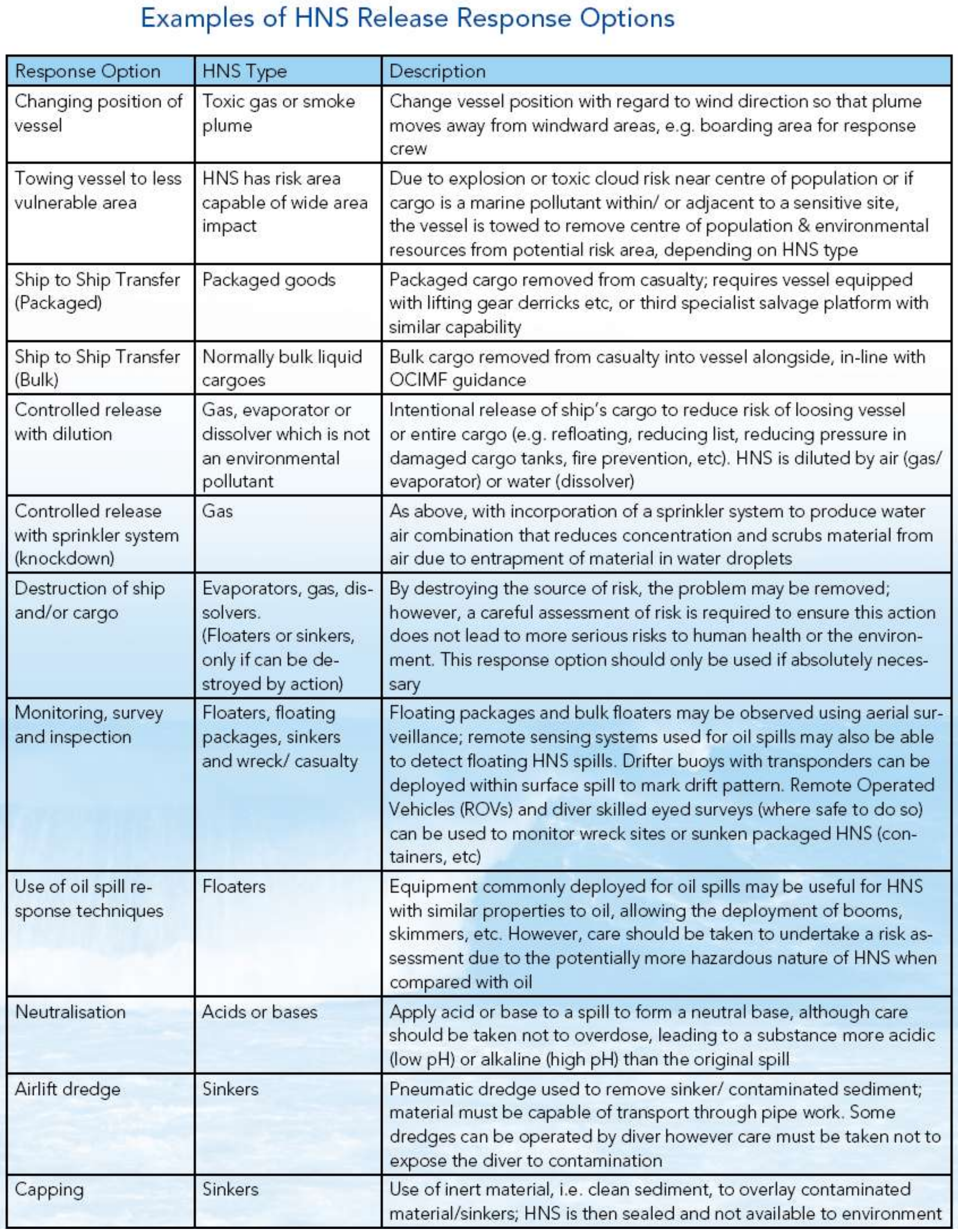
The **first priority** is always to **ensure the safety of those involved in the spill cleanup**. The **second priority** is **to remove as much as possible the pollutant without causing any further damage to the marine environment.**

Once an accidental spill occurs, the type and degree of damage to human health and marine environment will now be a matter of chance. The type and degree of damage depends partly on fortuitous circumstances and partly on the actions taken to minimise damage. Each spill will have its own detrimental effects in the aquatic environment. The damage may range from insignificant to catastrophic. The primary aims of a chemical substance spill response are to:

- **Protect human health and safety.**
- **Minimise environmental impacts.**
- **Restore the environment, as far as practically possible, to its pre-spill conditions.**

The range of counter pollution measures to be applied depends upon the location of the spill, type and quantity of the pollutant, the environmental sensitivity, and biodiversity of the area affected. Good management and planning, as well as the response actions put into effect by the responsible authority, will minimise the environmental impact of the chemical or hazardous substance spill.

Table 8. *Possible response actions in case of HNS spills*



Examples of HNS Release Response Options

Response Option	HNS Type	Description
Changing position of vessel	Toxic gas or smoke plume	Change vessel position with regard to wind direction so that plume moves away from windward areas, e.g. boarding area for response crew
Towing vessel to less vulnerable area	HNS has risk area capable of wide area impact	Due to explosion or toxic cloud risk near centre of population or if cargo is a marine pollutant within/ or adjacent to a sensitive site, the vessel is towed to remove centre of population & environmental resources from potential risk area, depending on HNS type
Ship to Ship Transfer (Packaged)	Packaged goods	Packaged cargo removed from casualty; requires vessel equipped with lifting gear derricks etc, or third specialist salvage platform with similar capability
Ship to Ship Transfer (Bulk)	Normally bulk liquid cargoes	Bulk cargo removed from casualty into vessel alongside, in-line with OCIMF guidance
Controlled release with dilution	Gas, evaporator or dissolver which is not an environmental pollutant	Intentional release of ship's cargo to reduce risk of loosing vessel or entire cargo (e.g. refloating, reducing list, reducing pressure in damaged cargo tanks, fire prevention, etc). HNS is diluted by air (gas/ evaporator) or water (dissolver)
Controlled release with sprinkler system (knockdown)	Gas	As above, with incorporation of a sprinkler system to produce water air combination that reduces concentration and scrubs material from air due to entrapment of material in water droplets
Destruction of ship and/or cargo	Evaporators, gas, dissolvers. (Floaters or sinkers, only if can be destroyed by action)	By destroying the source of risk, the problem may be removed; however, a careful assessment of risk is required to ensure this action does not lead to more serious risks to human health or the environment. This response option should only be used if absolutely necessary
Monitoring, survey and inspection	Floaters, floating packages, sinkers and wreck/ casualty	Floating packages and bulk floaters may be observed using aerial surveillance; remote sensing systems used for oil spills may also be able to detect floating HNS spills. Drifter buoys with transponders can be deployed within surface spill to mark drift pattern. Remote Operated Vehicles (ROVs) and diver skilled eyed surveys (where safe to do so) can be used to monitor wreck sites or sunken packaged HNS (containers, etc)
Use of oil spill response techniques	Floaters	Equipment commonly deployed for oil spills may be useful for HNS with similar properties to oil, allowing the deployment of booms, skimmers, etc. However, care should be taken to undertake a risk assessment due to the potentially more hazardous nature of HNS when compared with oil
Neutralisation	Acids or bases	Apply acid or base to a spill to form a neutral base, although care should be taken not to overdose, leading to a substance more acidic (low pH) or alkaline (high pH) than the original spill
Airlift dredge	Sinkers	Pneumatic dredge used to remove sinker/ contaminated sediment; material must be capable of transport through pipe work. Some dredges can be operated by diver however care must be taken not to expose the diver to contamination
Capping	Sinkers	Use of inert material, i.e. clean sediment, to overlay contaminated material/sinkers; HNS is then sealed and not available to environment

Decision-making systems must be based on the results from risk assessment and adequate information about:

(1) Hazard analysis (type of substance released, reaction ability, behavior, potential outflow, and potential impact)

(2) Response options (methods and techniques for minimising input and recovery of released substances; measures for maintaining safety of navigation; alerting measures for safety of adjacent populated areas; appropriate protection for response teams).

If it had been recognised that removal of the substance from the environment is not necessary or possible, then consideration should be given to establish a monitoring regime around the area likely to be affected. Objectives for monitoring should be to alert the authorities in case of a chemical release into the environment, to provide information on the extent of the release and the behavior of the chemical, and to measure its impact on the adjacent environment. Water, sediment, air, and biota might need to be sampled and analyzed depending on the circumstances, which will also dictate the necessary spatial and temporal distribution of the samples.

The aim of counter pollution action is to reduce or eliminate the hazardous effects of a spill. The selection of the most appropriate counter pollution action depends on the behavior and the dangers of the substance released. For measuring/detecting purposes, as well as for response, a distinction can be made among the following response categories:

1. Toxic gas clouds.
2. Toxic and explosive gas clouds.
3. Explosive gas clouds.
4. Flammable slicks.
5. Persistently/hindrance causing slicks on the water surface.
6. Toxic/carcinogenic clouds in the water column.
7. Persistently/hindrance causing pools on the sea floor.

Another category for response is “(Sunken) packaged goods or complete vessels containing chemicals”. This category is different from the seven mentioned above where the risk is associated with the substance and its behaviour. In this case, it has to do with the way hazardous substances accidentally entering the marine environment, irrespective of their characteristics and risks. They, therefore, will be dealt with separately. Each response category will be discussed in the following paragraphs.

7.2. Response Methods

Toxic and/or explosive gas clouds: This group of chemicals can rarely be combated at sea. Only ammonia gas cloud can be stopped in certain conditions by establishing a water fence. Response to this group of chemicals is mostly limited to reducing exposure to the chemicals by restricting access to the area of trajectory of the gas cloud. Appropriate computer models are needed to predict the size and the trajectory of such a gas cloud in combination with on- scene concentration measurements. The cloud can be made visible by giving it a color using specific reagents. When clouds are made visible, the exact position, dimensions, and tracks can be followed much more easily.

For **toxic gas clouds,** a comparison with the Maximum Allowable Concentration (MAC) values and Threshold Limit Values (TLV) of the substance(s) could be used as an indicator of its level of seriousness. If the concentration is less than 10% of the MAC/TLV, the situation can be assumed to be safe again. Use of protective clothing/breathing apparatus and (partial) evacuation can be considered as possible response options. When skin contacting with a dangerous substance is inevitable or likely to happen, preventive counter measures should be taken in the form of special body protective clothing. Breathing apparatus can be used for the protection of the respiratory organs if toxic gas is released. Breathing apparatus can be worn in combination with other protective clothing.

For **explosive gas clouds,** a comparison with the Lower Explosion Limit (LEL) value of the substance(s) could be used as an indicator of its level of seriousness. If the concentration is less than 1% of the LEL concentration, the situation can be assumed to be no longer volatile. All sources of ignition that can ignite flammable or explosive materials must be removed. This makes it impossible for explosion or combustion to take place. Possible sources of ignition are electric apparatus, hot surfaces, and naked flames and sparks. As a rule of thumb, when the concentration of gas in the air is over 1% of the LEL, care must be taken in order to avoid an explosion. The concentration at Selection of response measures which the gas cloud could be toxic is much lower than the concentration at which a gas cloud could be explosive.

Fire dangerous slicks: This group of chemicals can be combated with the so called first line oil recovery vessels. As this group of chemicals is under constant threat of fire and explosion, LEL needs to be continuously measured during the recovery actions. Due to evaporation, this kind of spill will disappear from the water surface after a period of time. In this sort of a spill, computer models are essential to predict the seriousness, the size, the potential trajectory of the slick, and the length of time it will take for the slick to disappear from the water surface if only partial recovery or no recovery takes place. Controlled combustion is a possibility to be considered if the substance layer is of sufficient thickness (> 3 mm). The risk associated with this method is high. The potential reaction should be recognised and people should maintain a safe distance from the source. The weather conditions should be suitable.

Sampling, monitoring, and calculations with the aid of models can estimate the size of the threatened area. Access to the polluted area has to be restricted as long as the concentration is higher than 1 % of the LEL value. Activities in the area, which can cause ignition, may also have to be restricted. Once the area was declared safe, the restriction should be lifted.

When skin contacting with a dangerous substance is inevitable or likely to happen, preventative counter measures should be taken in the form of special body protective clothing. It is safe to recover the substance when the concentration in the air measured on board of recovery vessel is less than 1% of the LEL. Anyone should never go into a polluted area (slick) when the gas concentration is too high, not even with a first line recovery vessel.

Persistent and hindrance causing slicks on the water surface: This group of chemicals can be combated with oil spill response methods such as skimmers, booms, and sweeping systems. For a safe recovery from a water surface of chemical substances with flash point < 61 є C, only vessels that comply with tanker regulations (so called first line of oil recovery vessels) should be used.

Due to the fact that floaters are invisible to the naked eye, remote sensing tools need to be used to detect such slicks on the water surface. In this type of situation, computer models are essential to predict the seriousness, the potential size and trajectory of the slick.

Mechanical recovery involves containment of the floating pollutant and removing it from the sea surface by means of skimmers and sweeping systems. In a case of very viscous or solid substances, netting should be used. Although there are many different types of skimmers and other recovery devices for removing oil from the water surface, the choice of response equipment depends on the type of chemicals (viscosity, corrosiveness, etc.) released.

Toxic/carcinogenic clouds in the water column: This group of chemicals, once released into the water and dissolved, could not be recovered at sea. Response to this type of chemicals has its own limitations. Reducing the exposure to toxic effects of the substance by restricting access to the trajectory area of the cloud is the most that can be done. In order to do this, an appropriate computer models which predict the size and trajectory of such a cloud in the water column, and the time period it will take to affect benthic habitats, combined with an on-scene measurements, are required. Very promising results have been reached with the use of bio monitor, using mussels to detect the substance dissolved in the water column. With the flow through Mussel Monitor, the seriousness of the spill can be detected on site.

The spill (cloud in the water column) can be given a color/tracer in order to make it visible. This can be done by using specific reagents. When clouds in the water column are made visible, the exact position, dimensions, and tracks can be assessed much more easily.

Sampling and calculations, with the aid of models, can estimate the size of the threatened area. Access to this area has to be restricted. Activities in the area may also have to be restricted. Once the area is declared safe, the restriction should be lifted.

Concentration of a toxic substance can have one of the following three effects on organisms:

- No effect. This level is normally taken as 1% of the LC50 (96).
- A sub lethal effect (for example, inhibition of growth).
- A lethal effect (LC50(96).

The effects on organisms depend on various factors (kind of organism, exposure time, conditions of organism, etc.). The situation can be assumed safe again when the concentration is less than

1% of the GESAMP B1 rating or the LC50 (96) of the substance involved. The toxic effect of a “Dissolver” will be more serious if the substance is bio accumulative and/or persistent (not easily biodegraded in the marine environment). The effects of a chemical in the marine environment are dependent on a combination of concentration and exposure time of organisms living in water. The higher the concentration the more serious the effect (e.g. bioaccumulation increases the concentration in exposed organisms and thus enhances the effects). The longer the exposure time the more serious the effect of the chemicals (e.g. chemicals, which are non-biodegradable or slow biodegradable, will last longer in the marine environment. Therefore, increasing the exposure time will result in more serious effects).

Persistent and hindrance causing pools on the sea floor: Substances in this group will stay on the sea floor providing some time to determine the best combating option. This group of chemicals can theoretically be combated with existing dredging equipment. The best solution for dealing with this category of sunken chemicals needs to be determined on an ad hoc basis. Availability, depth, type of substance, along with many other factors will determine which dredging tools will work best.

Dredging is usually described as a system for removal of underwater material. Therefore, it can be used as a response method for substances that are heavier than water. A choice can be made among hydraulic, mechanical, and pneumatic dredgers. The use of vacuum units is another alternative response method.

Detection of sunken substances could cause problems, as there are no particular detection techniques for sinkers. ROV and/or divers could be needed. Computer models could assist in locating the place where the sinker will rest.

Sampling and calculations, with the aid of computer models, can estimate the size of the threatened area. Access to the area has to be restricted. Activities in this area may also have to be restricted. Once the area is declared safe the restriction should be lifted.

Immobilization of a substance, by burying it, will prevent further movement of the substance. It is a mechanical method which leaves the substance in the environment. Therefore, the need to remove the substance from the seabed should be evaluated.

(Sunken) packaged goods or complete vessels containing chemicals: There are several salvage techniques for recovering packages and sunken vessels from the sea floor. It is not the substance in the package or the type of ship that determines the best response option, but rather factors such as water depth, strength of the package/ship, and current. As is the case with sunken substances (sinkers), major problem is the detection of packages on the sea floor. Once found, salvage companies could have the ability and the required skills to remove the packages. During salvage operations, one should always be prepared for the possibility that the packages/ships might break and that substances could be released into the marine environment. Depending on the category the substance(s) belongs to, one of the above- mentioned measures should be taken.

7.3. Sources of information on response methods

The original sources of information on HNS spill response can be found in various types of handbooks and databases. Very few manuals and handbooks in English specifically address the field of response to *maritime* accidents involving chemicals and dangerous goods. The followings are examples of such publications:

- HELCOM Response Manual, Volume 2.
- CHRIS Response Methods Handbook, US Coast Guard.
- Chemical Response Guide for 12 Chemicals- Operational Guides, CEDRE*.
- Containers and packages lost at sea - Operational Guide, CEDRE.
- Manual on Chemical Pollution -Section 1&2, IMO.
- Practical Guide for Marine Chemical Spills, REMPEC.

*The CEDRE (France Centre of Documentation, Research and Experimentation on Accidental Water Pollution) has elaborated detailed handbooks containing instructions for 12 selected substances (Annex B), and see also Annex C.

Annex A.

Property glossary

The properties listed are those which will provide an indication about environmental behavior, effects of a spilled chemical, and possible counter pollution actions.

Bioaccumulation We can distinguish two kinds of accumulation, reversible and irreversible accumulation. These terms state the manner in which the material is bound onto the tissue. With reversible accumulation, the material can be excreted again. With irreversible accumulation, the material is permanently bound to the organism. When the bond is reversible and the exposure is constant, a constant equilibrium concentration is established. There are two kinds of reversible accumulations distinguished by their method of uptake of the toxin. When a toxin is absorbed from the water phase, it is called bioaccumulation. The concentration can be described by the bioaccumulation factor. This factor is the quotient of the concentration in the organism and the concentration in the water column.

Flash point Flash point refers to the lowest temperature at which a liquid can still gives off enough vapor capable of ignition. The ignition source supplies certain amount of energy, which is necessary to heat an explosive or flammable vapour. When mixed locally, at a given temperature, it will produce an explosion or a fire. This local temperature is referred to as the ignition temperature, which is dependent on the oxygen concentration, time, pressure, and presence of catalysts.

GESAMP

A-value hazards profile The GESAMP bioaccumulation ratings are means of ranking the likelihood that particular substances become concentrated in living organisms.

+ = Bioaccumulative to a significant extent and known to produce a hazard to aquatic life or human health.

Z = Bioaccumulative with an attendant risk to aquatic organisms or human health, but with a short retention time of one week or less.

T = Bioaccumulative is liable to cause seafood tainted.

0 = No evidence to support anyone of the above ratings.

B-value hazards profile The GESAMP ratings for assessing damage to living resources specified are defined below.

	TLm 96h	
4 = highly toxic	< 1	mg/l
3 = moderately toxic	1- 10	mg/l
2 = slightly toxic	10- 100	mg/l
1 = practically non-toxic	100- 1000	mg/l
0 = non-hazardous	> 1000	mg/l
D = substance likely to blanket the seabed		
BOD = substance with oxygen demand		

C- value hazards profile The oral intake rating describes the hazards posed to human health due to the oral intake of certain substances. Three categories of hazard can be distinguished.

2 = hazardous

1 = slightly hazardous

0 = non-hazardous

E- value hazards profile The GESAMP reduction of amenities rating. The effects that substances are likely to have on the availability of amenities can be rated in the following manner:

*** = Highly objectionable because of persistence of smell or poison or irritant characteristics. As a result, beaches are liable to be closed. Rating is also used when there is clear evidence that the substance can cause cancer in human beings.

** = Moderately objectionable because of the above characteristics. Short term effects lead to temporary interference in the availability of the beaches. This rating is used when there is credible evidence that the substance is an animal carcinogen, and no clear evidence is available to suggest that the substance can cause cancer in human beings;

* = Slightly objectionable. No interference in use of beaches.

0 = No problems envisioned.

IMDG- Code Maritime Organisation Dangerous Goods (IMDG) Code. The International Maritime Organisation (IMO) approved a system of classifying chemical substances on the basis of physical hazards indentified at the International Conference on Safety of Lives at Sea in 1974. The IMO classification, given below, is an internationally recognised standard, which has been accepted virtually in all countries.

Class 1	**explosives**
Class 2	**gases: compressed, liquefied or dissolved under pressure**
Class 2.1	**inflammable gases**
Class 2.2	**non-inflammable gases**
Class 2.3	**poisonous gases**
Class 3	**inflammable liquids**
Class 3.1	**inflammable liquids: low flash point group. Flash point below -18°C, or possessing a low flash point in combination with other dangerous properties apart from being inflammable.**
Class 3.2	**inflammable liquids: intermediate flash point group. Flash point of -18°C, up to 23 °C**
Class 3.3	**inflammable liquids: high flash point group. Flash point of 23°C up to 61°C**
Class 4.1	**inflammable solids**
Class 4.2	**substances liable to have spontaneous combustion**
Class 4.3	**substances emitting inflammable gases when in contact with water**
Class 5.1	**oxidising substances (agents)**
Class 5.2	**organic peroxides**

Class 6.1	**poisonous (toxic) substances**
Class 6.2	**infectious substances**
Class 7	**radioactive substances**
Class 8	**corrosives**
Class 9	**miscellaneous dangerous substances**

LC(50) Lethal concentration fifty LC(50) is a calculated concentration which is expected to kill 50% of the population of experimental animals. Dosage is the most important factor in determining whether a given hazardous substance will produce a toxic effect. For comparisons of the toxicity of different hazardous substances, the median lethal concentration LC(t)50 (t = 96 hours, is normally used as a yardstick. The higher the LC (t)50 value, the lower the hazard.

Description	LC(96)50 values	
Highly toxic	< 1	mg/l
Moderately toxic	1 - 10	mg/l
Slightly toxic	10 - 100	mg/l
Practically non-toxic	100 - 1000	mg/l
Non-hazardous	> 1000	mg/l

Mortality of an organism is a clear measure. With experiments, the percentage of a specific kind of organism that dies within a certain time can be measured. LC-50 (96) , for example , is the Lethal Concentration for 50 % of the test organisms die within 96 hours. Other percentages (n) and exposure times (t) are possible (LC-n (t)).

LEL The Lower Explosion Limit (LEL) is the minimum percentage of vapor (gas) at which a vapor or gas mixture can be made to explode. Below the lower explosion limit, reaction only takes place when there is a continuous supply of external heat. In the case of concentrations above the lower explosion limit, combustion might occur.

MAC The Maximum Allowable Concentration (MAC) of a substance given in ml/m3 = ppm or g/m3 is defined as the maximum concentration of that substance in ppm of air in which people can work safely for a period of eight hours, five days a week.

Minimum hazard	- substances with a MAC	>500 ppm
Some hazard	- substances with a MAC	>100 <500
Moderately hazardous	- substances with a MAC	>10 <100
Severely hazardous	- substances with a MAC	<10 ppm

For substances with a very low MAC value, one should be very careful even if the substance is not classified as "Evaporator"

Marine pollution category

The GESAMP hazard categories provide a basis on which to assess the severity of marine pollutants. Three categories can be distinguished, ranging from X to Z, in descending order of importance.

Category X:	**Substances which are bioaccumulative and highly toxic to aquatic life**
Category Y:	**Substances which are moderately toxic to aquatic life**
Category Z:	**Substances which are slightly toxic to aquatic life**
Category OS:	**Substances which are practically non-toxic to aquatic life, or which cause seabed to be covered with deposits.**

No Effect Level

When a toxicity experiment for sub- lethal effects is done, it is possible to find the so called “No Effect Level”. The 96 hour LC50 gives an indication of the concentration which, if exceeded, would be lethal. This is available for a wide range of chemicals and can be used to predict likely safe concentrations. When a chemical, spilled in the marine environment, is neither persistent nor bioaccumulative, acute chronic, or sub-lethal effects are rarely found in organisms at concentrations of less than 0.01 times the 96 hour LC50 to the test species. In the absence of counter- indications, 1% of the LC50 can be taken as a “safe” with No Effect Level (N.E.L). (see also No Observed Effect Level).

No Observed Effect Level

No Observed Effect Level (N.O.E.L). It is possible to apply a conservative safety factor of 0.01 in translating acute L.C.(50) value to life cycle no- adverse effect level. This still provides a large margin of safety between exposure limits and effect levels. (See also “No Effect Level”).

Octanol-water partition coefficient

The ratio of concentration of the chemical at equilibrium in octanol, in water phase, is related to bioaccumulation. The experience with a wide variety of organic compounds indicate that if this partition coefficient exceeds 1000, the probability of measurable bioaccumulation in aquatic species will be high. Often this is expressed in Pow, the logarithm of the octanol/water partition coefficient, which gives an indication on the lipophylity rate of a chemical. When a chemical has a Pow larger than 3 or 4 (1000 or 10 000 as it is the Logarithm), it is able to pass the liphophyd membranes of the cells and accumulate in the fat resources. Not only bioaccumulation, but also sediment bonding can be described with the Pow values. A high rate of bonding to the sediment is related to the high Pow.

Relative gas density The densities of the common gaseous products, transported by sea, are mostly given in kg/m3. By comparing the density of a particular gas with that of air (1.29

kg/m3), an estimate can be made of whether the substance will rise into the atmosphere or remain on the water surface. The value obtained is equal to the ratio of the weight of a given volume of vapor to the weight of an equal volume of dry air, in the same temperature and pressure conditions. Using the ratio M/29, where M is the molecular weight of the substance concerned, following approximate is used.

TLM(96) Tolerance Limit median, See LC50

highly toxic	TLm less than 1	mg/l
moderately toxic	TLm 1 - 10	mg/l
slightly toxic	TLm 10 - 100	mg/l
practically non toxic	TLm 100 - 1000	mg/l
non-hazardous	TLm more than 1000	mg/l

TLV Threshold Limit Values refers to an airborne concentration of a product expressed in parts per million in the air. This is the time-weighted concentration believed to be safe for the average person during an 8-hour workday and 40-hour working week for prolonged periods. The equilibrium concentration of a gas, which can be produced by a liquid, can be calculated as follows:

Concentration (ppm) = vapor pressure in mm of Hg x 1300 or

Concentration (ppm) = vapor pressure in Pa x 9.75

If concentrations are higher than three times the TLV level, warnings should be issued for possible health risks for people in the area of dissemination, accompanied with advices on what actions to take.

Annex B. LIST CEDRE's Operational Manuals

(given as an example)

ETHYL ACRYLATE

E.U. Classification:

F: Highly flammable

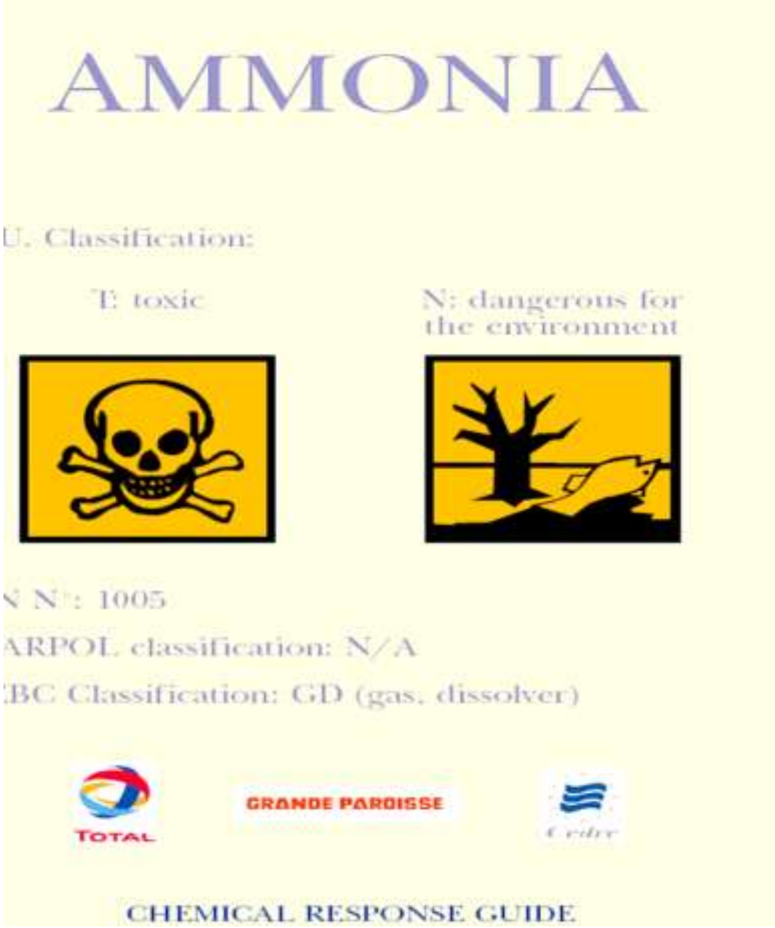
Xn: Harmful

UN N°: 1917 (stabilised)

SEBC Classification: ED (evaporates/dissolves)

MARPOL classification: A until 31/12/2006
Y from 01/01/2007

CHEMICAL RESPONSE GUIDE



AMMONIA

U. Classification:

T: toxic

N: dangerous for the environment

N N°: 1005

ARPOL classification: N/A

BC Classification: GD (gas, dissolver)

CHEMICAL RESPONSE GUIDE

BENZENE

E. U. Classification:

F: Readily flammable

T: Toxic

UN N°: 1114

MARPOL classification: C until 31/12/2006
Y from 01/01/2007

SEBC classification: E (Evaporator)

ATOFINA TOTAL Cedre

CHEMICAL RESPONSE GUIDE

DIMETHYL DISULPHIDE

EU classification:

F: Highly flammable

Xn: Harmful

N: Dangerous for the environment

UN n°: 2381

MARPOL classification: Y
SEBC classification: S (sinks)

CHEMICAL RESPONSE GUIDE

1,2-Dichloroethane

UN N°: 1184

SEBC Classification: S/D (Sinker/Dissolver)

MARPOL classification: B until 31/12/2006
Y from 01/01/2007

E.U. Classification:

F: Highly flammable

T: Toxic

ARKEMA

TOTAL

Cedre

CHEMICAL RESPONSE GUIDE

1,2-Dichloroethane

UN N°: 1184

SEBC Classification: S/D (Sinker/Dissolver)

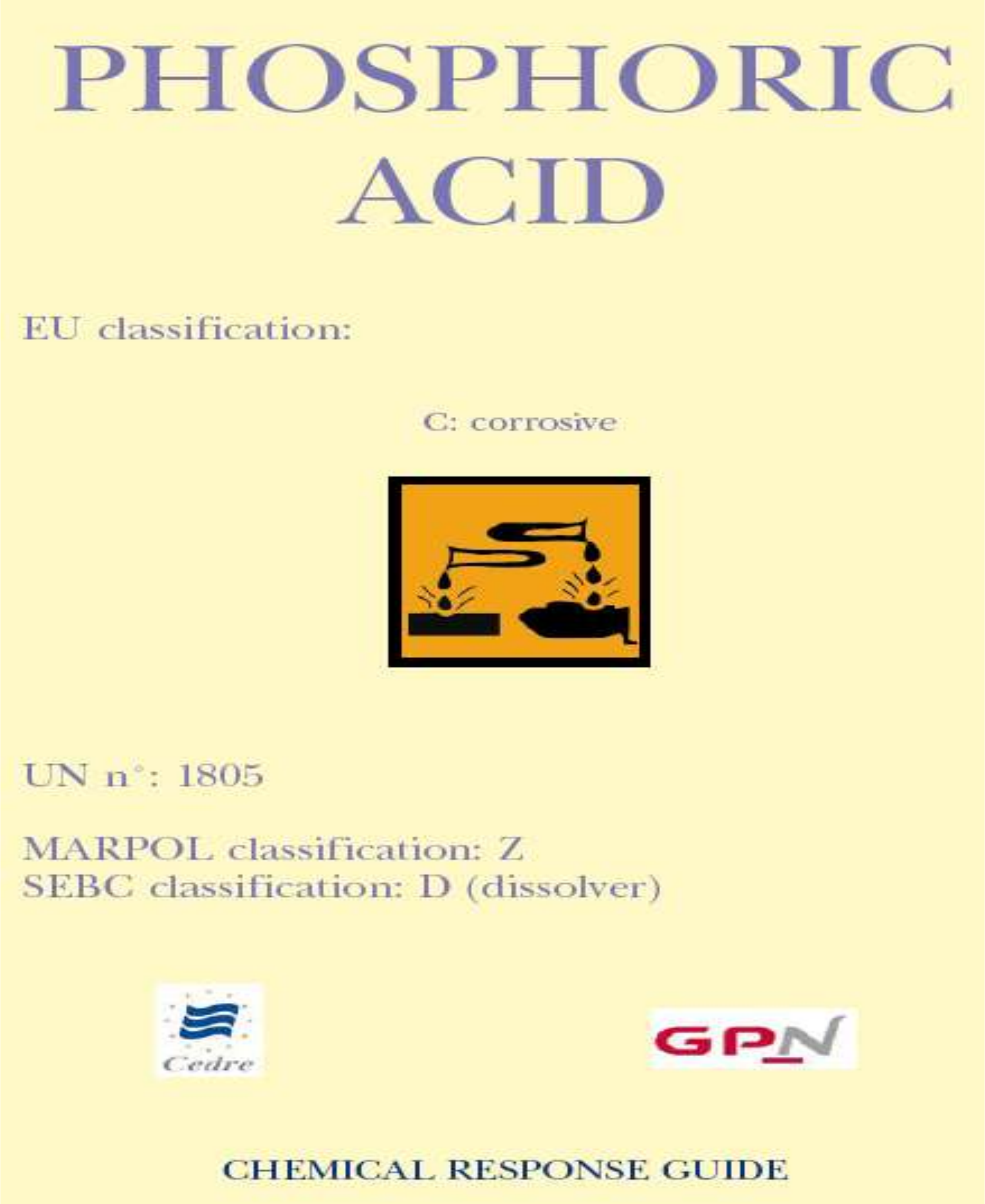
MARPOL classification: B until 31/12/2006
Y from 01/01/2007

E.U. Classification:

F: Highly flammable

T: Toxic

CHEMICAL RESPONSE GUIDE



PHOSPHORIC ACID

EU classification:

C: corrosive

UN n°: 1805

MARPOL classification: Z
SEBC classification: D (dissolver)

CHEMICAL RESPONSE GUIDE

STYRENE

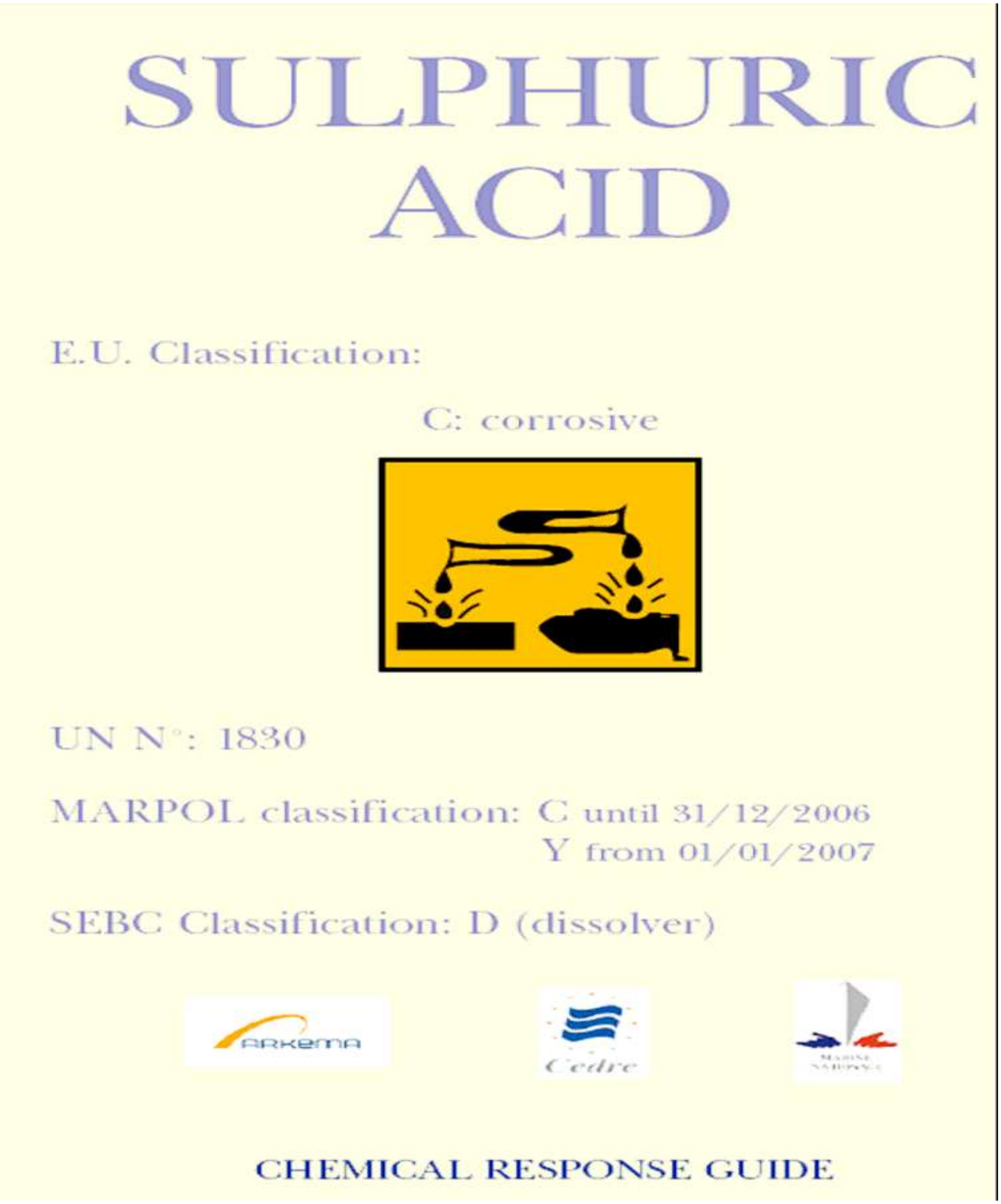
E.U. classification: Xn Noxious

UN N°: 2055

MARPOL classification: B until 31/12/2006
Y from 01/01/2007

SEBC classification: Floater/Evaporator

CHEMICAL RESPONSE GUIDE



SULPHURIC ACID

E.U. Classification:

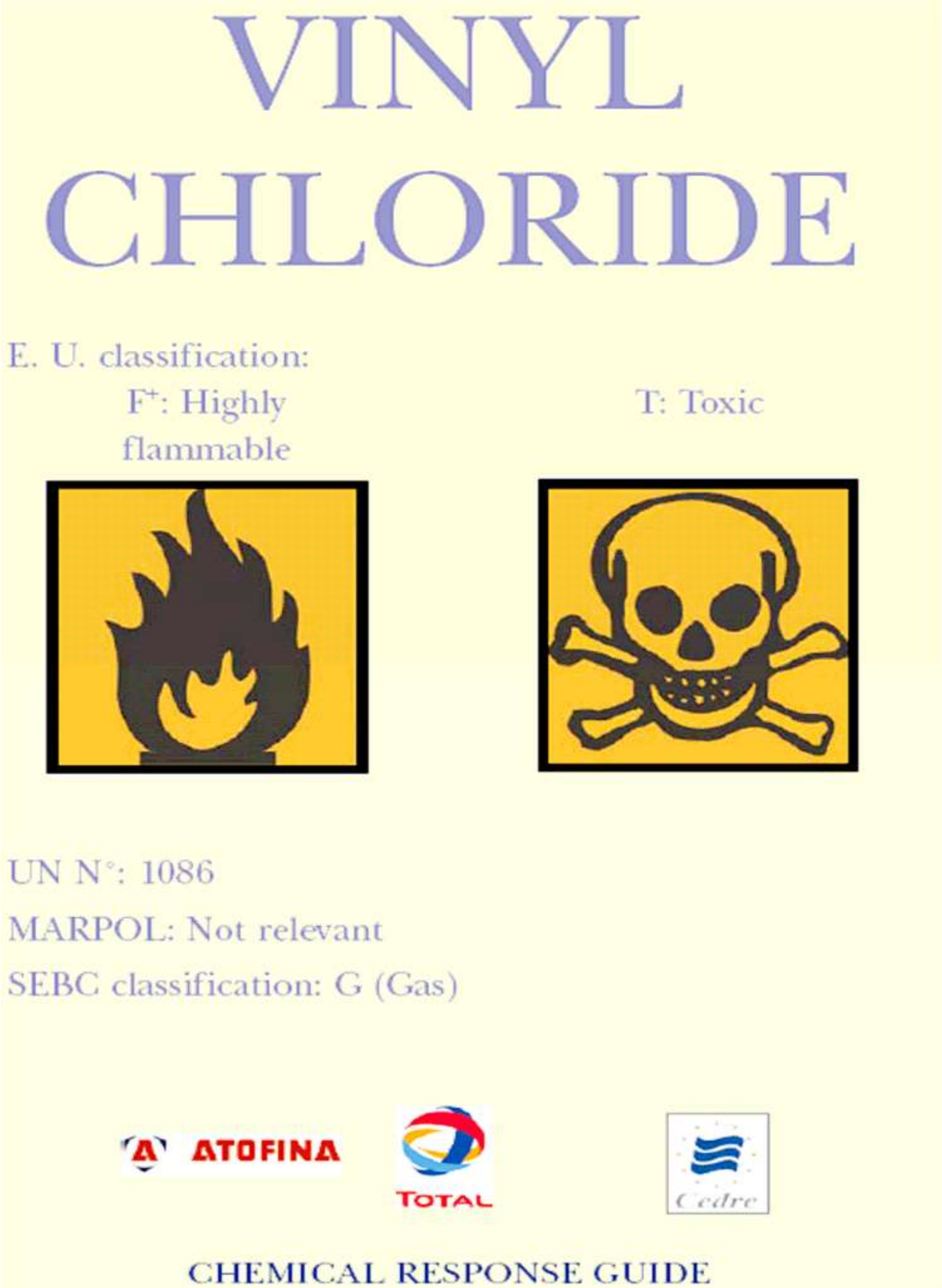
C: corrosive

UN N°: 1830

MARPOL classification: C until 31/12/2006
Y from 01/01/2007

SEBC Classification: D (dissolver)

CHEMICAL RESPONSE GUIDE



VINYL CHLORIDE

E. U. classification:

F$^+$: Highly flammable

T: Toxic

UN N°: 1086

MARPOL: Not relevant

SEBC classification: G (Gas)

ATOFINA

TOTAL

Cedre

CHEMICAL RESPONSE GUIDE

XYLENES

EU Classification:

Flammable Xn: Harmful

UN n°: 1307 (o-xylene, p-xylene)
3295 (mixed xylenes)

MARPOL classification: Y
SEBC classification: FE (floats and evaporates)

TOTAL TOTAL PETROCHEMICALS Cedre

CHEMICAL RESPONSE GUIDE

SODIUM HYDROXIDE 50% SOLUTION

E.U. Classification:

C: corrosive

UN N°: 1824

MARPOL classification: D until 31/12/2006
Y from 01/01/2007

SEBC Classification: D (dissolver)

TOTAL ARKEMA Cedre

CHEMICAL RESPONSE GUIDE

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